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Textile Dyeing Wastewaters Characterization and Treatment

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TEXTILE DYEING WASTEWATERS: CHARACTERIZATION AND TREATMENT

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Textile Industry	Carbon	Stationary Sources	11E	
Dyeing	Biological Treatment	Total Organic Carbon	13H	06C
Waste Water	Chemical Engineering	TOC Removal		07A
Properties	Ozone		14B	
Treatment	Alums			
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TEXTILE DYEING WASTEWATERS: CHARACTERIZATION AND TREATMENT

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ABSTRACT

Treatability of wastewaters from selected typical dye baths by biological, chemical and physical means was examined. Twenty systems were selected to provide a broad cross section of dye classes, fibers and application techniques. Wastes were produced using typical formulations on a pilot plant scale to provide desired control and simulate plant conditions. Raw wastes were characterized. Treated wastes were evaluated for color and TOC. Biological treatability at several concentrations was examined without seed, with domestic sewage and acclimated seed. Wastes generally were compatible with the biological process; color reduction was incomplete. No single treatment was effective for both color and TOC removal. Chemical treatment with ozone decolorized the wastes. Physical treatments were done with alum, lime and activated carbon using jar tests. Disperse, vat and sulfur dyes were most effectively decolorized by coagulation procedures and carbon was most effective for decolorizing reactive, basic, acid and azoic dyes. A statistical evaluation of heavy metal content of dye baths and a compendium of dye bath additives and dyeing methods is included.

This report was submitted in fulfillment of Grant Number R803174 by the American Dye Manufacturers Institute under the partial sponsorship of the Environmental Protection Agency. Work was completed as of September 1975. This work covers a period from June 30, 1974 to December 29, 1975. Work was completed in September, 1975.

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LIST OF ABBREVIATIONS AND SYMBOLS

ABBREVIATIONS

ADMI	--American Dye Manufacturers Institute
APHA	--American Public Health Association
AWWA	--American Water Works Association
BOD and BOD_5	--five day biochemical oxygen demand
C.I. Name	--Color Index generic name
COD	--chemical oxygen demand
EPA	--United States Environmental Protection Agency
FWPCA	--Federal Water Pollution Control Act
g	--gram
g/l	--grams per liter
N.B.S.	--National Bureau of Standards
NH_3-N	--ammonia nitrogen
nm	--nano meter
NO_2-N	--nitrite nitrogen
NO_3-N	--nitrate nitrogen
NO_2/NO_3-N	--nitrite-nitrate nitrogen
PAC	--powdered activated carbon
Pt-Co	--platinum cobalt color standard
Scfh	--standard cubic feet per hour
S.D.	--standard deviation
TKN	--total kjeldahl nitrogen
TOC	--total organic carbon
UNC	--University of North Carolina at Chapel Hill
WPCF	--Water Pollution Control Federation
μg/l	--micrograms per liter
μm	--micrometer

SYNBOLS

$\sim$	--approximately
$<$	--less than
$>$	--more than
$\leq$	--less than or equal to
$\geq$	--more than or equal to
$\cong$	--approximately equal to

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The dyeings required for the study were performed at North Carolina State University under the direction of Mr. Gene Floyd. The fabric, dyes and chemicals used were supplied by the members of the American Textile Manufacturers Institute and the American Dye Manufacturers Institute.

The treatability studies were performed at the University of North Carolina at Chapel Hill under the direction of Dr. Philip C. Singer and Dr. Linda W. Little.

The analyses of the mill samples were performed in the laboratories of several members of the American Dye Manufacturers Institute. Coordination of the analytical effort and the preparation of the summary were under the direction of Dr. Harshad Vyas of Verona Division of Mobay Chemical Corporation. Individuals assisting in this effort include Mr. Thomas Alspaugh of Cone Mills, Mr. William Martin of Martin Marietta Chemicals, Mr. James Gouch of Allied Chemical Corporation, Dr. J. Robert Martin of E. I. duPont de Nemours and Company, Inc., Mr. John Murphy of ICI America, Mr. Roger Rounds of GAF Corporation and Dr. Janos Schultze of Ciba-Geigy Corporation.

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SECTION I

INTRODUCTION

BACKGROUND

In 1970, the American Dye Manufacturers Institute undertook a program to meet an increasing need for information concerning dyes in the environment. This effort took the form of both "in-house" work and study grants to several universities. The "in-house" work produced a study of the heavy metal contents of dyes and an improved method for the measurement of color in solutions. The work at the universities included studies of the effects of 46 dyes on aerobic and anaerobic systems and on fish. All of this work was published by ADMI in Dyes and the Environment, Volume I,[1] (September 1973).

This work was continued with a grant which provided for a study of the effects of an additional ten dyes on fish,[2] and a study of the effects of all 56 dyes on algae[2]. The 9 dyes most likely to be a burden on the environment were studied in pilot plant secondary treatment systems in order to ascertain both the effect of the dye on the treatment system and the effect of the treatment on the dye. Effluent from these pilot plant systems was studied for its effect on fish[2]. A Masters thesis which examines the effects on fish and algae of a variety of anthraquinone dyes is included with this work[2]. These studies were published by ADMI in Dyes and the Environment, Volume II,[2] (September 1974).

THE PRESENT WORK

This report documents a continuation of these earlier studies. It examines the treatability of twenty selected wastewaters from dye baths and extends the study of heavy metals in dyes to a survey of the heavy metal content of the wastewater from commercial dye baths. A compendium is included as an aid to those not familiar with the art of dyeing and to provide a reference to the many varieties of additives commonly used in dye baths. The report is rich in raw experimental data in order that it might prove valuable to users. The variety and complexity of commercial dyeing practice is such that it is more appropriate to present detailed data than to generalize the data and limit its usefulness. A primary objective of the study is to provide a preliminary assessment of which treatment methods might be most useful for each of the various wastewaters examined.

THE DYEING SYSTEMS

The parameters of greatest significance in providing real variety to dyeing systems are the fiber dyed, the application class of the dye used and the application method. The twenty dyeing systems were selected so as to provide a broad representation of actual practice in dyeing and to include as much variation of the three significant parameters as possible. Fibers represented in the twenty systems include cotton, rayon, wool, polyamide, polyester and polyacrylic. Yarn, woven, knit and carpet constructions are represented. The application classes of dyes used are acid, basic, direct, reactive, vat, disperse, sulfur, naphthol, direct developed, 1:2 and 1:4 acid premetallized, acid chrome and after copperable direct. Application methods include: beck, package machine, continuous range and Kuester range.

The dyeings, except for the Kuester application, were all accomplished in pilot scale equipment at North Carolina State University. This provided the means to exercise good control over the variables and to simulate commercial practice. The Kuester application was accomplished in the laboratory of an ADMI member, also on a pilot scale.

Wastewaters from the dye baths were transported to the University of North Carolina at Chapel Hill for characterization and treatability studies. Additional samples were provided to ADMI for heavy metals and benzidine analyses.

BIOLOGICAL TREATABILITY

Biological systems are in common use throughout the textile industry and many wastewaters from this industry have been shown to be treatable by this method. The present study examines the treatability of wastewaters from only the dye bath, in order to provide insight into the impact of an individual dye bath on the biological system and to examine the efficiency of the application of biological treatment. In practice, wastewaters from dye baths are diluted appreciably with other process wastes and rinse waters.

The wastewaters were treated at full strength and in two dilutions in systems using seed from a combined domestic/industrial waste activated sludge plant and acclimated seed. A control with Hg(II) added was used to distinguish between biological and nonbiological changes. The treatment was carried on for 21 days and samples were periodically removed for examination.

PHYSICAL TREATMENT SYSTEMS

Alternative techniques to biological treatment that may be applicable to wastewater from dye baths include coagulation or precipitation, carbon adsorption and oxidation. Coagulants used included lime, aluminum salts and ferric salts. Various types of powdered activated carbon were used. Oxidation investigations were limited to ozonation.

Standard jar test procedures were used to evaluate the treatability of the wastewaters with the coagulants and with carbon. Ozonation was accomplished by passing oxygen through an ozone generator and treating the samples in a gas-liquid contactor at a controlled gas flow rate. The ozone content of the applied gas stream was measured analytically to determine the application rate. All of the physical-chemical studies were performed at full strength of the wastewater. Combined biological and selected physical-chemical treatment was examined for three of the wastewaters.

TEXTILE MILL EFFLUENT SURVEY

Earlier work by ADMI[1] showed that the heavy metal content of non-metallized dyes was less than 100 ppm. The objective of this study is to evaluate the contribution of heavy metals to textile mill effluents from the dyeing operation.

This was accomplished by sampling dye bath wastewaters from selected mill dyeing operations and analyzing them for cadmium, chromium, copper, lead, mercury and zinc.

Benzidine has been a recent cause for concern. For this reason, analyses for benzidine were run on these same samples to provide a preliminary assessment of benzidine concentrations over a wide range of wastewaters from dyeing operations.

THE COMPENDIUM

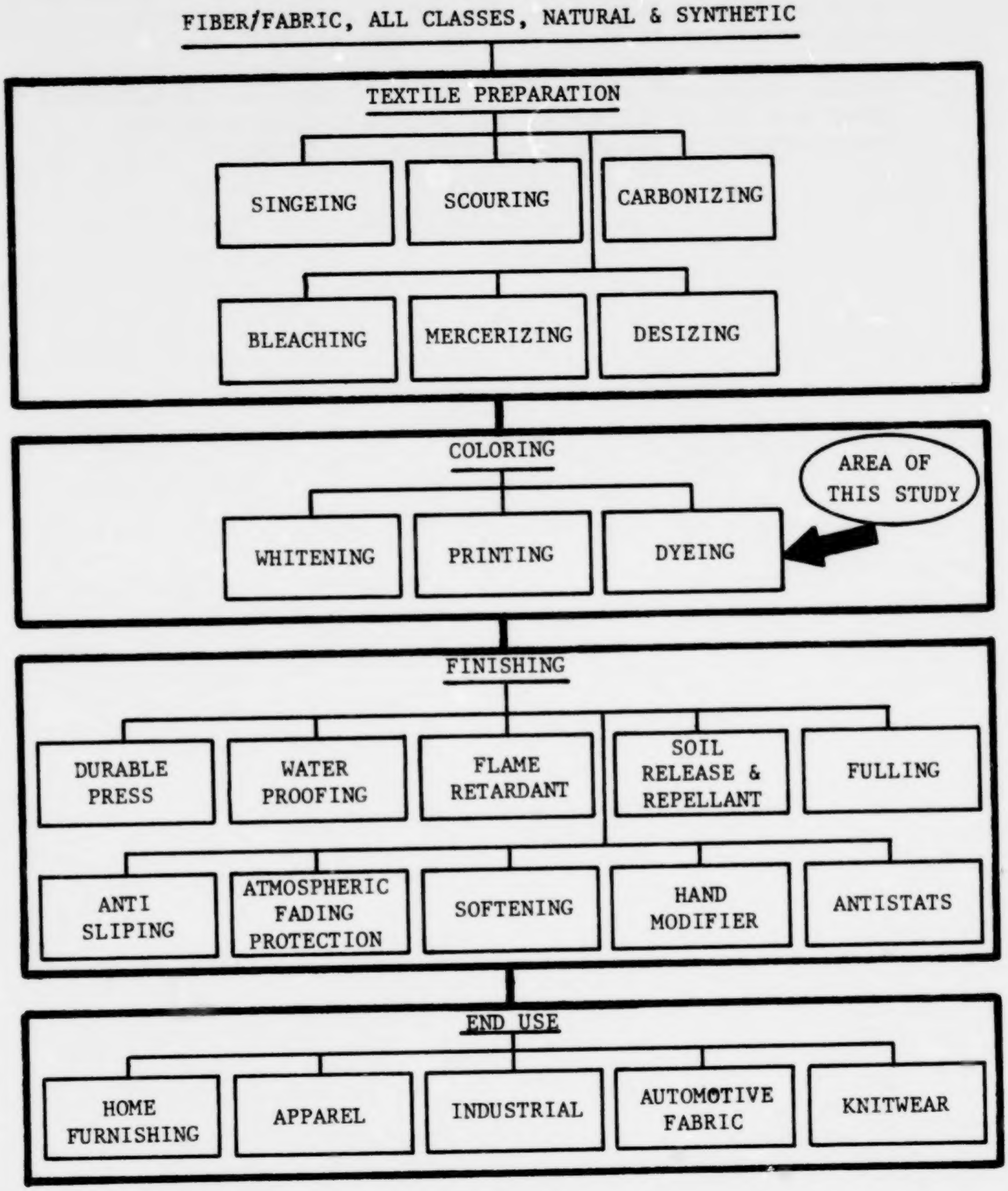
The compendium included in this report provides a convenient reference to commercial dyeing techniques for those not familiar with this art. Included in the compendium is a tabulation classifying common additives to dye baths according to chemical type. This is intended as a resource that can be used along with the description of the dyeing systems in Section IV to gain some insight into the chemicals likely to be present in dye baths. This tabulation is not intended to be exhaustive but is rather an illustrative supplement to Section IV.

Table I is a flow chart depicting many of the processing steps through which fibers or fabrics may pass in preparing them for various end uses. The particular processing step of concern in this study is marked. Most of the additional steps noted on the chart also produce waste effluent and consideration of the total effluent from textile processing operations must necessarily account for these steps. While every textile mill does not utilize every processing step indicated, most use a number of them, thus contributing to the complexity of treating textile mill effluent.

THE APPENDICES

Information relative to the analytical protocols used in this study have been included in the appendices.

FIGURE 1. TEXTILE PROCESSING FLOW CHART


FIBER/FABRIC, ALL CLASSES, NATURAL & SYNTHETIC
TEXTILE PREPARATION
SINGEING
SCOURING
CARBONIZING
BLEACHING
MERCERIZING
DESIZING
COLORING
AREA OF THIS STUDY
WHITENING
PRINTING
DYEING
FINISHING
DURABLE PRESS
WATER PROOFING
FLAME RETARDANT
SOIL RELEASE & REPELLANT
FULLING
ANTI SLIPING
ATMOSPHERIC FADING PROTECTION
SOFTENING
HAND MODIFIER
ANTISTATS
END USE
HOME FURNISHING
APPAREL
INDUSTRIAL
AUTOMOTIVE FABRIC
KNITWEAR

REFERENCES

1. ADMI. Dyes and the Environment: Reports of Selected Dyes and Their Effects, Volume I., American Dye Manufacturers Institute. September 1973.

2. ADMI. Dyes and the Environment: Reports of Selected Dyes and Their Effects, Volume II., American Dye Manufacturers Institute. September 1974.

SECTION II

CONCLUSIONS

1. Dyeing wastewaters can be effectively treated with respect to BOD, TOC, and color removal if they can be segregated in-plant.
2. No one specific type of treatment will suffice for all dyeing wastewaters; the most effective type of treatment depends upon the type of dyeing performed and the chemical composition of the dye bath.
3. Disperse, vat, and sulfur dyeing wastewaters can be readily decolorized by coagulation with alum but are not readily decolorized by activated carbon.
4. Reactive, basic, acid, and azoic dyeing wastewaters can be readily decolorized by activated carbon; basic dyes are more strongly adsorbed on carbon than reactive dyes.
5. Reactive dyes can be decolorized most effectively by ozone; disperse dyes are decolorized least by ozone.
6. BOD and TOC removal by physical-chemical treatment techniques, i.e., coagulation, carbon adsorption, and ozonation, is not very effective.
7. The organic constituents of the dyeing wastewaters are relatively biodegradable and BOD and TOC can be effectively reduced by biological treatment.
8. BOD removal is, generally, not inhibited by the dye molecules or other components of the dye bath.
9. Color, in general, is not readily removed by biological waste treatment, suggesting that the dye molecules are not readily biodegradable.
10. Some dyeing wastewaters are capable of inhibiting biological nitrification, but the causative agents of the inhibitory action have not been identified.
11. Dyeing wastewaters can be effectively treated with respect to BOD, TOC, and color removal by coupling biological treatment with physical-chemical treatment methods, the former to remove BOD and TOC and the latter to remove color.
12. The heavy metal content of exhausted dye baths is low except in those cases where a heavy metal is used for oxidation (e.g. Chromium) or for after treatment (e.g. Copper).
13. Dyeing wastewaters generally contain low suspended solids.

SECTION III

RECOMMENDATIONS

1. Among the different application classes of dyes investigated, disperse, vat and sulfur dyes have been shown to be readily removed from dyeing wastewaters by coagulation; basic, acid, azoic, and reactive dyes are readily removed by activated carbon adsorption; reactive dyes are more easily decolorized by ozone than are disperse dyes. Laboratory-scale studies should be continued to determine which chemical classes among the different application classes of dyes are most effectively removed by these physical-chemical treatment techniques, e.g. among the basic dyes, which chemical classes (azo, anthraquinone, thiazole, indophenol, etc.) are most strongly adsorbed on activated carbon. This could provide a useful criterion for selection of dyes in commercial applications.

2. This study has shown, on a bench-scale batch basis only, that dyeing wastewaters can be effectively treated for the removal of BOD, TOC, and color. The results of this study should be applied on a continuous-flow pilot-scale basis in order to confirm the conclusions regarding the best type of treatment, to establish design and operational criteria (e.g. mixing requirements for flocculation basins, overflow rates for settling tanks, loadings and contact times for carbon columns, etc.) for most efficient treatment, and to develop cost information to achieve desired levels of performance.

3. Modifications of dyeing procedures should be investigated to select methods and system components which provide more effective adsorption of the dyes by the substrate and which minimize the concentrations of potential pollutants in the effluent from the dye bath, e.g. kjeldahl-nitrogen, BOD and TOC, dissolved solids, etc.

SECTION IV

DYEING SYSTEMS

This project is designed to provide a meaningful preliminary measure of the contribution of commercial textile dyeing operations to the pollution burden of dyeing and finishing plants, and to evaluate a variety of waste-treatment procedures for removal of the many different pollutants. Textile dyeing technology, in the broad sense, is multidimensional and extremely complex. Many fiber substrates, several types of process equipment, hundreds of chemically different dyes, and a large number of dye bath auxiliary chemicals are used routinely. The evolution of textile dyeing from an "art" to modern processes subject to precise engineering, and even computer control, has been in process for a very few years and is not yet complete. It was necessary, therefore, to select very carefully the dyeing systems to be used in this study to insure that the small number of samples permitted by available time and funding would yield the maximum amount of information which would be truly representative of commercial practice.

The twenty dyeing systems described later in this chapter were defined by a panel of five men representing many decades of practical experience in dye and textile dyeing technology. These systems reflect all the major fiber substrates, representative dye types (from the standpoint of both chemical types and application classes), and major dye bath auxiliary types. While pilot plant equipment used in the actual dyeing experiments does not provide scale-down models of all major dyeing equipment, this should not significantly affect the representative character of the dye bath wastes.

Fibers utilized include cotton, rayon, wool, polyamide (including three chemical variants receptive to different dye classes), polyacrylic, and one intimate blend of cotton and polyester. Different fibers were processed as yarn, woven fabric, knit fabric and tufted carpet. Thirty-seven dyes included representatives of direct, after coppered direct, developed direct, acid, 1:2 and 1:1 metallized acid, vat, reactive, naphthol, sulfur, disperse and basic classes. Representative dyeing processes included both batch and continuous operations.

Dyeing experiments were carried out in pilot plant equipment under close supervision of Mr. Gene G. Floyd, North Carolina State University, Raleigh, N. C. Combined residual dye bath, scour and rinse water from individual batch processes, and combined scour and rinse water from individual continuous processes were conveyed without delay to University of North Carolina at Chapel Hill, N. C., for wastewater treatability studies under direction of Drs. Philip C. Singer, and Linda W. Little. Samples of these effluents also were submitted to selected industry laboratories (ADMI member companies) for spectral characterization and determination of benzidine and selected heavy metals.

Procedures used in the selected dyeing operations are detailed in the following section. Unless otherwise specified, percentages given are based on the weight of fiber. Additional information on dye bath auxiliaries and specific dyes employed follow the dyeing procedures is shown in Tables 1 and 2. The sequence of dyeing processes investigated is arbitrary and is numbered in the actual sequence.

Table 1. DYES USED IN DYEING PROCEDURES

Application class	C. I. name
Acid	Acid Black 52 Acid Blue 7 Acid Blue 40 Acid Blue 122 Acid Blue 298 Acid Red 145 Acid Red Acid Yellow 198
Basic	Basic Blue 92 Basic Blue 41 Basic Red 23 Basic Red 73 Basic Yellow 11 Basic Yellow 31
Developer	Developer 1 Direct Black 38 Direct Blue 160
Disperse	Disperse Blue 56 Disperse Blue 62 Disperse Blue 87 Disperse Brown 2 Disperse Orange 41 Disperse Red 55 Disperse Violet 28 Disperse Yellow 3 Disperse Yellow 42
Fiber Reactive	Reactive Red 40 Reactive Red 120
Insoluble Azo	Azoic Diazo Component 13
Mordant Acid	Acid Black 11
Naphthol	Azoic Coupling Component 7
Sulfur	Sulfur Black 1

Table 1 (continued). DYES USED IN DYEING PROCEDURES

Application class	C. I. name
Vat	Vat Black 13 Vat Black 25 Vat Blue 18 Vat Green 3 Vat Orange 2

Table 2. AUXILIARIES USED IN DYEING PROCEDURES

Commercial name	Use	Chemical nature
Alkanol A-CN	nonionic surfactant	ethylene oxide condensate
Alkanol ND	anionic surfactant	sodium aryl sulfonate
Alkanol WXN	anionic surfactant	modified sodium alkylaryl sulfonate
Aritex AD	anionic surfactant	sodium long-chain alcohol sulfate
Avitone T	anionic surfactant	sodium hydrocarbon sulfonate
Barisol BRM	anionic surfactant	phosphated long-chain alcohol
Calgon	Water softener	$NaPO_3$
Capracyl Leveling Salt	nonionic surfactant	ethylene oxide condensate
Carolid FLM	carrier	emulsified ortho-phenylphenol
Carolid 3F	carrier	nonionic, modified biphenyl derivative
Chemocarrier KD5W	carrier	self emulsifiable solvent, nonionic
Compound 8S	anionic surfactant	complex diaryl sulfonate
Duponol FAS	foaming agent	anionic surfactant composition
Irgaformal S2E	antiform agent	blend of hydrocarbons, terpens, silicone, emulsifier
Levegal KN	leveling agent	oxethylated fatty acid derivative

Table 2 (continued). AUXILIARIES USED IN DYEING PROCEDURES

Commercial name	Use	Chemical nature
Ludigol	anti-reducing agent	sodium m-nitrobenzene sulfonate
Merpol DA	nonionic surfactant	ethylene oxide condensate
Merpol HCS	nonionic surfactant	ethylene oxide condensate
Merpol ST	nonionic surfactant	ethylene oxide condensate
Mesitol NBS	after treating agent	
Orvus K Paste	anionic surfactant	long-chain alcohol sulfate
Product BCO	amphoteric surfactant	cetyl betaine
Retarder HP	retarder for cationic dyes	cationic compound
Sequestrene ST	sequestrant for calcium, copper, iron	tetrasodium salt of sequestrene AA
Sodyefide B	liquid reducing agent	Na_2S and Na_xS in solution
Syngum D-47-D	thickener for carpet dyeing	natural gum derivative
Superclear 100N	thickener	natural gum
Tanalon Jet	carrier for pressure dyeing polyester	modified self-emulsifiable solvents
Versene	sequestrant	EDTA

DYEING PROCEDURE NO. 1

DYES: Vat

PROCEDURE: Package Dyeing - Exhaust

EQUIPMENT: Gaston County - 35 pound package dyeing machine

MATERIAL: 15 one-pound packages
Mercerized cotton yarn

LIQUOR RATIO: 15:1

DYEING PROCEDURE:
Set bath at 100° F. with:
2.0% Compound 8-S
10.0% Caustic soda
5.0% C.I. Vat Blue 18
3.5% C.I. Vat Black 13
1.0% C.I. Vat Orange 2
Circulate five minutes
Raise temperature 3° F. per minute to 180° F. Continue to circulate bath for 20 minutes (cycle machine 4 minutes inside-out; 4 minutes outside-in)
Cool bath to 140° F. and add:
10.0% sodium hydrosulfite (1/2 inside-out; 1/2 outside-in)
Circulate for 30 minutes reversing cycle each 4 minutes.
Drop bath

Rinse: Give two cold rinses - (original volume)

Oxidize:
Set bath at 110° F. with 1.0% acetic acid (56%)
Circulate 5 minutes, add:
2.0% sodium perborate
Raise bath to 140° F.
Run 10 minutes
Raise bath to 190° F.

Soaping:	1.0% Avitex AD (surfactant) 0.5% tetrasodium pyrophosphate Run 10 minutes at 190° F. Drop bath
Rinse:	Give two cold rinses (original volume)
Extract:	Hydro Extractor
Dry:	Oven

DYEING PROCEDURE NO. 2

DYES:	Acid - 1:2 metal - complex
PROCEDURE:	Exhaust
EQUIPMENT:	Rodney Hunt - 20" Sample Dye Beck
MATERIAL:	Polyamide Tricot
LIQUOR RATIO:	30:1
DYEING PROCEDURE:	Set bath at 100° F. with the following: 1.0% Capracyl leveling salt (non-ionic surfactant) 4.0% ammonium acetate 5.0% sodium sulfate 20.% C.I. Acid Black 52 Bath pH 6.5 Circulate fabric for 10 minutes at 100° F. Raise temperature in 45 minutes to 205° F. Run at 205° F. for 60 minutes Cool to 140° F.
Rinse:	Give one cold rinse (original volume)
Dry:	Clip Tenter Frame

DYEING PROCEDURE NO. 3

DYES: Disperse

PROCEDURE: Atmospheric Exhaust

EQUIPMENT: Rodney Hunt - 20" Sample Dye Beck

MATERIAL: Polyester texturized double knit

LIQUOR RATIO: 30:1

DYEING PROCEDURE: Set bath at 120° F. with:
1.0g/l Compound 8-S (surfactant)
5.0g/l Carolid FLM (ortho-phenylphenol carrier)
1.0% acetic acid (56%) to pH of 5.4
3.0% C.I. Disperse Blue 87
1.0% C.I. Disperse Yellow 42
1.0g/l Compound 8-S (surfactant)
Raise temperature of bath to 212° F. in 40 minutes
Dye at 212° F. for 90 minutes
Cool to 160° F.
Drop bath

Rinse: Give one rinse (original volume)

Scour: Scour at 160° F. for 10 minutes with:
1.0g/l Merpol HCS (surfactant)
1.0g/l soda ash
1.0g/l sodium hydrosulfite
Drop bath

Rinse: Rinse at 160° F. (original volume)
Rinse at 120° F. (original volume)

Dry: Clip Tenter Frame

DYEING PROCEDURE NO. 4

DYES:	After-copperable direct
PROCEDURE:	Exhaust
EQUIPMENT:	Rodney Hunt 20" Sample Dye Beck
MATERIAL:	Bleached mercerized cotton
LIQUOR RATIO:	30:1
DYEING PROCEDURE:	Add to bath: 0.5 g/l soda ash (pH 8.5) 0.5% Barisol BRM (anionic surfactant) 0.5% Calgon (sequestrant) Circulate for 10 minutes at 120° F. and add dye 4.0% C.I. Direct Blue 160 Circulate 10 minutes Raise temperature in 30 minutes to 200° F. Run 15 minutes at 200° F. then add: 30.0% salt - (calcium and magnesium free) in 4 portions over 15 minutes Run at 200° F. for 45 minutes Cool to 160° F. Drop bath
Rinse:	Give cold rinse (original volume)
After Treatment:	2.0% acetic acid (56%) 2.0% copper sulfate crystals Circulate at 100° F. for 5 minutes Raise temperature to 160° F. Run at 160° F. for 20 minutes Drop bath
Rinse:	Give two cold rinses (original volume each)
Dry:	Clip Tenter Frame

DYEING PROCEDURE NO. 5

DYES:	Reactive
PROCEDURE:	Exhaust
EQUIPMENT:	Rodney Hunt 20" Sample Dye Beck
MATERIAL:	Bleached, mercerized cotton
LIQUOR RATIO:	20:1
DYEING PROCEDURE:	Set bath at room temperature with: 2.0 g/l Ludigol (anti-reducing agent) 3.0% C.I. Reactive Red 120 Raise temperature to 120° F. and hold for 10 minutes, then add: 100.0 g/l salt (calcium and magnesium free) Add salt in 4 portions over 40 minutes while raising temperature to 175° F. Dye at 175° F. for 20 minutes, then add: 20 g/l soda ash 1.2 g/l caustic soda Run at 175° F. for 50 minutes Drop bath
Rinse:	Cold rinse (original volume) Drop bath Hot rinse at 150° F. (original volume) Drop bath
Soaping:	Set bath at 100° F. with: 1 g/l Barisol BRM (anionic surfactant) 1 g/l soda ash Run bath for 15 minutes at 212° F. Cool to 160° F. Drop bath
Rinse:	Give hot rinse at 150° F. (original volume) Give cold rinse (original volume)
Dry:	Clip Tenter Frame

DYEING PROCEDURE NO. 6

DYES: Disperse

PROCEDURE: Exhaust

EQUIPMENT: Rodney Hunt 20" Sample Dye Beck

MATERIAL: Polyamide tufted carpet

LIQUOR RATIO: 20:1

DYEING PROCEDURE: Set bath at 100° F. with:
0.5% Avitone T (Anionic surfactant)
1.0% Merpol DA (nonionic surfactant)
0.5% Versene 100 (sequestrant)
Circulate 5 minutes and add dyes:
0.22% C.I. Disperse Yellow 3
0.075% C.I. Disperse Red 55
0.006% C.I. Disperse Violet 28
Add trisodium phosphate (pH 9.0-9.5)
Raise temperature to 190-200° F. over 45 minutes
Dye one hour
Cool bath to 160° F. and drop

Rinse: Give one rinse at 110° F. (original volume)

Dry: Clip Tenter Frame

DYEING PROCEDURE NO. 7

DYES:	Acid
PROCEDURE:	Exhaust
EQUIPMENT:	Rodney Hunt 20" Sample Dye Beck
MATERIAL:	Wool Fabric
LIQUOR RATIO:	30:1
DYEING PROCEDURE:	Set bath at 100° F. and add: 2.0% Acetic acid (56%) 5.0% anhydrous sodium sulfate 5.0% C.I. Mordant Black 11 Circulate for 10 minutes at 120° F. Raise temperature in 30 minutes to 212° F. Run at 212° F. for 30 minutes, then add: 2.0% formic acid (pH 3.5-4) Run for 30 minutes at 212° F. Cool to 170° F.; add: 3.0% sodium bichromate Raise temperature rapidly to 212° F. Run at 212° F. for 30 minutes Cool to 140° F. Drop bath
Rinse:	Give two warm rinses (120° F.) (original volume) Drop bath
Dry:	Clip Tenter Frame

DYEING PROCEDURE NO. 8

DYES: Basic

PROCEDURE: Exhaust

EQUIPMENT: Rodney Hunt 20" Sample Dye Beck

MATERIAL: Acrylic fabric

LIQUOR RATIO: 30:1

DYEING PROCEDURE:
Set bath at 100° F. and add:
10.0% anhydrous sodium sulfate
2.0% acetic acid (56%) pH 4.5
2.0% Retarder HP (cationic retarder)
Circulate for 10 minutes at 120° F. then add:
3.0% C.I. Basic Red 23
Circulate 10 minutes at 120° F.
Raise temperature in 45 minutes to 190° F.
Hold at 190° F. for 15 minutes
Raise temperature to 212° F. at 1° F. per minute
Run at 212° F. for 60 minutes
Cool to 140° F. at 4° F. per minute
Drop bath

Rinse:
Give two warm rinses 110° F. (original volume)
Drop bath

Dry: Clip Tenter Frame

DYEING PROCEDURE NO. 9

DYE: Disperse

PROCEDURE: Atmospheric Exhaust

EQUIPMENT: Rodney Hunt 20" Sample Dye Beck

MATERIAL: Tufted carpet

LIQUOR RATIO: 30:1

DYEING PROCEDURE:
Set bath at 110° F. with
0.25% Irgaformal S 2 E (antifoam agent)
1.0% Calgon
1.0% monosodium phosphate
0.5% acetic acid (56%) pH 4.5-5.0
Circulate 10 minutes, then add over a 10 minute period the following:
1.5% C.I. Disperse Yellow 42
1.5% C.I. Disperse Blue 87
0.5% Compound 8-S (surfactant)
Raise temperature to 160° F. at 3° F. per minute, then add over 15 minute period:
10.0% Carolid 3F (biphenyl carrier)
Run 10 minutes at 160° F.
Raise temperature to 212° F. at 3° F. per minute, then add over 15 minute period:
10.0% Carolid 3F (biphenyl carrier)
Run 10 minutes at 160° F.
Raise temperature to 212° F. at 3° F. per minute
Run at 212° F. for 90 minutes
Cool to 160° F.
Drop bath

Rinse:
Give hot rinse 160° F. for 10 minutes (original volume)
Drop bath

Post Scour:
Set bath at 100° F. and add:
1.0% Merpol DA (nonionic surfactant)
1.0% trisodium phosphate
1.0% sodium hydrosulfite
Raise temperature to 160° F. and run for 15 minutes
Drop bath

Rinse:	Give two warm rinses 120° F. (original volume) Drop bath
Dry:	Clip Tenter Frame

DYEING PROCEDURE NO. 10

DYE: Acid

PROCEDURE: Atmospheric Exhaust

EQUIPMENT: Rodney Hunt 20" Sample Dye Beck

MATERIAL: Polyamide filament, circular knit

LIQUOR RATIO: 30:1

DYE PROCEDURE:
Set bath at 100° F. with:
1.5% Alkanol ND (anionic surfactant)
20.% acetic acid (56%) pH 5-5.5
5.0% anhydrous sodium sulfate
Circulate for 10 minutes, then add
3.0% C.I. Acid Blue 40
Circulate 10 minutes
Raise temperature to 208° F. in 45 minutes
Run at 208° F. for 60 minutes
Cool to 140° F.
Drop bath

Rinse:
Give cold rinse (original volume)
Drop bath

After treatment:
Set bath at 100° F. with
2.0% acetic acid (56%) pH 4.4.5
5.0% Mesitol NBS (after-treating agent)
Circulate for 5 minutes
Raise temperature rapidly to 200° F.
Run at 200° F. for 20 minutes
Cool to 140° F.
Drop bath

Rinse: Give one cold rinse (original volume)

Dry: Clip Tenter Frame

DYEING PROCEDURE NO. 11

DYES:	Direct
PROCEDURE:	Exhaust
EQUIPMENT:	Rodney Hunt 20" Sample Dye Beck
MATERIAL:	Rayon
LIQUOR RATIO:	30:1
DYEING PROCEDURE:	Set bath at 100° F. with: 1.0 g/l Levegal KN (leveling agent) Circulate for 10 minutes and add 4.0% C.I. Direct Black 38 Raise temperature to 120° F. and circulate for 10 minutes Raise temperature to 200° F. over 30 minutes and add: 20.0% sodium sulfate Add salt over a 30 minute period Run at 200° F. for 60 minutes Cool to 160° F. Drop bath
Rinse:	Give two cold rinses (original volume) Drop bath
Dry:	Clip Tenter Frame

DYEING PROCEDURE NO. 12

DYES:	Direct-Develop
PROCEDURE:	Exhaust
EQUIPMENT:	Rodney Hunt 20" Sample Dye Beck
MATERIAL:	Rayon
LIQUOR RATIO:	30:1
DYEING PROCEDURE:	Set bath at 100° F. with: 1.0 g/l Levegal KN (leveling agent) Circulate for 10 minutes and add 4.0% C.I. Direct Black 38 Raise temperature to 120° F. and circulate for 10 minutes Raise temperature to 200° F. over 30 minutes and add: 20.0% sodium sulfate Add over a 30 minute period Run at 200° F. for 60 minutes Cool to 160° F. Drop bath
Rinse:	Give two cold rinses (original volume)
Diazotizing Bath:	Set bath at 80° F. and add 3.0% sodium nitrite Circulate for 5 minutes, then add: 7.5 hydrochloric acid 20° Bé Run 20 minutes at 80° F. Drop bath
Rinse:	Give three cold rinses
Develop:	Set bath at 80° F. and add: 1.5% Developer Z Run for 20 minutes at 100° F. Drop bath
Rinse:	Give three cold rinses

Scour:	Set bath at 100° F. and add: 0.5% Barisol BRM (surfactant) Heat bath to 130° F. and run for 10 minutes Drop bath
Rinse:	Give two warm rinses at 120° F. Drop bath
Dry:	Clip Tenter Frame

DYEING PROCEDURE NO. 13

DYE: Basic, disperse and acid

PROCEDURE: Exhaust

EQUIPMENT: Rodney Hunt 20" Sample Dye Beck

MATERIAL: Carpet of nylon styling yarn

LIQUOR RATIO: 30:1

DYEING PROCEDURE: Set bath at 80° F. with:
0.25% Alkanol A-CN (surfactant)
0.25% trisodium phosphate
1.0% monosodium phosphate (pH 6.0-6.2)
0.25% Sequestrene ST (sequestrant agent)
Circulate bath for 10 minutes, then add the below dyes over a ten-minute period:
0.5% C.I. basic Red 73
0.1% C.I. Basic Blue 92
Run for 5 minutes, then add the following dyes over a five-minute period:
0.3% C.I. Disperse Yellow 3
0.1% C.I. Disperse Red 55
0.02% C.I. Disperse Blue 7
0.5% C.I. Acid Red 145
1.20% C.I. Acid Blue 122
0.10% C.I. Acid Yellow 198
Run 10 minutes
Raise temperature to 205° F. at 2° F. per minute
Check pH and adjust to 6.0-6.2
Dye for 60 minutes at 205° F.
Cool bath to 140° F.
Drop bath

Rinse: Give two cold rinses 70-80° F.
Drop bath

Dry: Clip Tenter Frame

DYEING PROCEDURE NO. 14

DYE:	Disperse
PROCEDURE:	High temperature exhaust
EQUIPMENT:	35 Pound Gaston County Package dye machine
MATERIAL:	Polyester yarn 15-1 lb. packages
LIQUOR RATIO;	8:1
DYEING PROCEDURE:	Set bath at 120° F. with 1.0 g/l Compound 8-S (Anionic surfactant) 4.0% Tanalon Jet (carrier) 1.0% acetic acid (56%) pH = 5-6 Circulate 10 minutes, and add 4.0% C.I. Disperse Blue 56 Dye was pasted up with equal amount of the above surfactant Raise temperature to 250° F. in 45 minutes Dye at 250° F. for 60 minutes Cool to 160° F.
Rinse:	Give one rinse at 100° F. for 5 minutes Drop bath
Scour:	Set bath at 100° F. and add 1.0 g/l caustic soda 1.0 g/l sodium hydrosulfite 1.0 g/l Product BCO (surfactant) Run at 160° F. for 10 minutes Drop bath
Rinse:	Give one rinse at 160° F. for 5 minutes Give one rinse at 120° F. for 5 minutes
Dry:	Oven

DYEING PROCEDURE NO. 15

DYE:	Sulfur
PROCEDURE:	Continuous (pad-chemical pad-steam-wash-oxidize)
EQUIPMENT:	Continuous dye range
MATERIAL:	Bleached mercerized cotton
WET PICKUP:	80%
DYEING PROCEDURE:	
Padding:	Pad fabric at 110° F. with quick immersion using: 180 g/l C.I. Sulfur Black 1 22.5 g/l Sodyefide B (sodium sulfide) 2.0 g/l Penetrant SCA (surfactant)
Steaming:	60 sec. at 214° F.
Rinsing:	1st wash box - cold 2nd wash box - cold
Oxidation:	3rd wash box 7.5 g/l hydrogen peroxide 7.5 g/l acetic acid (56%) at 140° F.
Rinsing:	4th wash box - 140° F.
Soaping:	5th wash box 2.0 g/l Orvus K Paste (surfactant) at 180° F.
Rinsing:	6th wash box - 140° F.
Dry:	Dry cans

NOTE: 100 yards of fabric was used on continuous dye range.
120 liters of solution used in each wash box.

DYEING PROCEDURE NO. 16

DYE: Reactive

PROCEDURE: Continuous (pad-dry-thermofix-wash-dry)

EQUIPMENT: Pad-Tenter Frame - Continuous Dye Range

MATERIAL: Bleached mercerized cotton

WET PICKUP: 80%

DYEING PROCEDURE:

Padding:
40.0 g/l C.I. Reactive Red 40
75.0 g/l urea
3.0 g/l Ludigol (anti-reducing agent)
20.0 g/l soda ash
20.0 g/l Superclear 100N (thickener)
Padding temperature 100° F.

Dry: 225° F.

Fixation: Thermofix at 330° F./90 seconds

Rinse:
1st wash box - cold
2nd wash box - cold
3rd wash box - 160° F.

Soaping: 4th wash box - 2.0 g/l Barisol BRM (anionic surfactant) at 200° F.

Rinse:
5th wash box - 180° F.
6th wash box - cold

Dry: Dry cans

NOTE: 100 yards of fabric was used in this dyeing.
120 liters of solution used in each wash box.

DYEING PROCEDURE NO. 17

DYES: Vat/Disperse

PROCEDURE: Thermosol - Pad - Steam

EQUIPMENT: Pad-Tenter Frame - Continuous Dye Range

MATERIAL: 50/50 Polyester/cotton

WET PICKUP: 70%

DYEING PROCEDURE:

Padding:
Pad to 70% wet pick-up with:
32.0 g/l C.I. Disperse Blue 62
16.0 g/l C.I. Disperse Orange 41
6.4 g/l C.I. Disperse Brown 2
22.0 g/l C.I. Vat Green 8
16.5 g/l C.I. Vat Black 25
15.0 g/l C.I. Vat Green 3
15.0 g/l Superclear 100N (thickener)
1.0 g/l Alkanol WXN (surfactant)

Dry: Predry fabric at 250° F.

Thermosol: Thermosol at 410° F. for 90 seconds

Chemical Pad:
60.0 g/l caustic soda
60.0 g/l sodium hydrosulfite at 80% wet pick up

Steam: Steam fabric 45 seconds at 214° F.

Rinse:
1st wash box - cold
2nd wash box - cold

Oxidation:
3rd wash box
4.0 g/l Hydrogen peroxide
4.0 g/l acetic acid (56%)
30 seconds exposure at 140° F.

Rinse: 4th wash box - 140° F.

Soaping:
5th wash box
2.0 g/l Orvus K Paste (surfactant) at 200-210° F.

Rinse: 6th wash box - 140° F.

Dry: Dry cans

DYEING PROCEDURE NO. 18

DYES:	Basic
PROCEDURE:	Atmospheric Exhaust
EQUIPMENT:	Rodney Hunt 20" Sample Dye Beck
MATERIAL:	Polyester "Dacron" T-92
LIQUOR RATIO:	30:1
DYEING PROCEDURE:	Set bath at 120° F. with: 1.0% acetic acid (56%) pH 5 5.0% sodium sulfate Circulate 10 minutes, then add 1.5% C.I. Basic Blue 41 1.5% C.I. Basic Yellow 11 Heat bath to 160° F. at 2° F. per minute, then add: 5.0 g/l Chemocarrier KD5W (carrier) Circulate 10 minutes Raise temperature in 25 minutes to 212° F. Run at 212° F. for 60 minutes Cool slowly to 160° F. Drop bath
Rinse:	Give two rinses at 120° F. 5 minutes each rinse (original volume)
Dry:	Clip Tenter Frame

DYEING PROCEDURE NO. 19

DYES: Basic, disperse, acid

PROCEDURE: Kuster, Continuous

EQUIPMENT: Kuster carpet dye range

MATERIAL: Nylon Carpet T-844/T-845/T-847

WET PICKUP: Wet out 110%, padding 400%

DYEING PROCEDURE:

Wet Out:
Wet out carpet in:
2.0 g/l Merpol ST (surfactant) at 130° F.

Pad Bath:
2.5 g/l Syngum D-47-D (thickener)
1.0 g/l Alkanol A-CN (surfactant)
1.0 g/l Duponol F.A.S. (foaming agent)
0.60 g/l C.I. Basic Yellow 31
0.2 g/l C.I. Acid Blue 298
0.02 g/l Stylacyl Red RB
0.20 g/l C.I. Disperse Blue 7
Pad bath temperature at 80° F.
Running speed - 5 yards per minute

Steam: 8 minutes at 212° F.

Rinse:
Rinse at 75° F.
Give three rinses at this temperature in 40:1 bath rinses

Dry:

DYEING PROCEDURE NO. 20

DYES: Naphthol

PROCEDURE: Exhaust

EQUIPMENT: Gaston County 35 pound package dye machine

MATERIAL: Bleached cotton yarn 15-1 lb. packages

LIQUOR RATIO: 8:1

DYEING PROCEDURE:
Prepare machine at 85° F. with:
5.0% caustic soda
Run at 110° for 10 minutes, add
2.0% Naphthol AS-SW solution
1/2 solution inside out
1/2 solution outside in
Run 30 minutes at 130° F., then add:
10.0% salt
Run 15 minutes
Drop bath - drain machine

Salt Rinse:
Make up solution of:
8 oz/gal salt
Add to machine and run 10 minutes at 60° F.
Drop bath - drain machine completely

Coupling Bath:
Make up solution of:
8.0% Fast Scarlet R salt
1.0% acetic acid (56%)
Add solution to machine and run cold in machine for 30 minutes
Drop bath

Rinse:
Raise temperature to 170° F. over 20 minutes
Drop bath

Soaping:	2.0% Product BCO (surfactant) 2.0% soda ash 0.5% oz/gal Calgon Raise temperature to 200° F. Run 20 minutes Cool to 180° F. Drop bath
Rinse:	Give three rinses at 75° F. each rinse 5 minutes each rinse
Extract:	Hydro Extractor
Dry:	Oven

SECTION V

CHARACTERIZATION OF DYEING WASTEWATERS

Dyeing wastewaters were generated at North Carolina State University at Raleigh. Small aliquots (1/2 gallon) of each wastewater were preserved and sent to member companies of ADMI for analysis of the selected trace metals including cadmium, chromium, copper, lead, mercury, and zinc and for analysis of benzidine and phenols in wastewaters. Samples for trace metal analysis were preserved, handled and analyzed according to EPA approved methods.[1] Samples for benzidine analysis were preserved by addition of 25 ml of conc. HCl per liter of sample. Samples preserved for trace metal analysis were also used for phenolics analysis.

Wastewaters were transported in stainless steel containers to the UNC Wastewater Research Center in Chapel Hill. There they were stored under refrigeration until use. Wastewaters were mixed thoroughly with a mechanical stirrer before sampling. As soon as possible after arrival samples of wastewater were removed for raw wastewater characterization by the methods indicated in Table 3. An exception to this was the BOD[a] analysis which was delayed until an acclimated seed was developed (10 days).

Results from analysis of dyeing wastewaters for trace metals, benzidine, and phenols are given in Table 4. A summary of the other raw wastewater characteristics is presented in Table 5.

Generally, cadmium, chromium, and copper were found to be present in amounts less than 0.1 mg/l. Notable exceptions are dyeing wastewaters no. 2 and no. 7 for chromium, and no. 4 for copper. In dyeing system no. 2, chromium is present in the dye as a part of the dye molecule. System no. 7 uses a mordant dye that requires after-chroming with 3.0% sodium dichromate. System no. 4 uses after-copperable direct dye requiring 2.0% copper sulfate in the dye bath.

Lead and zinc were found to be present in amounts smaller than 1.0 mg/l. Mercury was generally present in quantities lower than the detection limit of 0.5 μg/l. Phenols were observed, in most systems, in quantities of less than 0.5 mg/l. Phenols in higher quantities can all be explained by the use of carriers, based on phenolics, in dyeing systems.

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[a] All BOD references are to BOD_5

TABLE 3. ANALYTICAL PROCEDURES

Parameter	Procedure	Reference
Benzidine	Adaption of chloramine-T oxidation procedure	See Appendix
BOD_5, total	YSI DO Analyzer (Probe)	APHA, AWWA, WPCF, 1971[3]
" , soluble	As above, after filtration	
Chloride	(1) Specific ion probe	Orion technical literature
"	(2) Mercuric nitrate titration	APHA, AWWA, WPCF, 1971[3]
Color	ADMI procedure	ADMI, 1973[2]
Nitrogen, NH_4^+	Automated phenolate	FWPCA, 1969[4]
" NO_3^-	Automated hydrazine reduction	FWPCA, 1969[4]
" NO_2^-	Automated diazotization	FWPCA, 1969[4]
" TKN	Automated digestion and then automated phenolate	FWPCA, 1969[4]
pH	Electrometric	APHA, AWWA, WPCF, 1971[3]
Phenolics	4-aminoantipyrine with distillation	EPA, 1974[1]
Phosphorus, total	Persulfate digestion followed by atuomated $SnCl_2$ method	FWPCA, 1969[4]
Solids, suspended	Gooch crucible filtration, 103°C (Method 224 C)	APHA, AWWA, WPCF, 1971[3]
" dissolved	Gravimetric, 103°C	APHA, AWWA, WPCF, 1971[3]
TOC, total	Dow-Beckman Carbonaceous Analyzer, Model 915 (Dual Channel)	FWPCA, 1969[4]
" soluble	As above, after filtration	FWPCA, 1969[4]
Trace metals	See Appendix	EPA, 1974[1]

TABLE 4. ANALYSIS OF DYEING SYSTEMS WASTES

Dyeing Procedure Number	Metal Content in mg/l					Mercury µg/l	Phenol mg/l	Benzidine µg/l
	Cadmium	Chromium	Copper	Lead	Zinc			
1	0.02	<0.01	0.05	<0.01	0.12	<0.5		
2	0.01	1.59	0.01	0.10	0.05	<0.5		
3	<0.01	<0.01	0.01	0.02	0.02	2.0	23.9	
4	0.21	0.11	17.0	0.10	0.06	3.0	0.07	
5	0.09	0.12	0.10	0.08	0.17	<0.5	0.01	
6	0.01	0.05	0.05	0.06	0.16	<0.5	0.02	
7	0.01	38.3	0.11	0.08	0.84	<0.5	0.02	
8	<0.01	0.01	0.05	<0.01	0.17	<0.5	0.06	<10
9	0.02	<0.01	0.04	0.20	0.18	<0.5	0.24	16
10	0.01	<0.01	0.08	0.08	0.23	<0.5	0.13	<10
11	0.01	<0.01	0.04	<0.10	0.40	<0.5	0.40	7.6
12	0.01	<0.01	0.41	<0.10	0.31	<0.5	0.50	<10
13	0.01	0.01	0.10	0.20	0.15	<0.5	0.02	4.2
14	<0.01	0.02	0.12	<0.10	0.61	<0.5	0.61	7.6
15	<0.01	0.01	0.72	<0.05	0.36	<0.5	0.02	<10
16	<0.01	<0.01	0.07	<0.05	0.09	<0.5	0.05	<10
17	0.01	0.21	0.88	0.05	0.66	<0.5	0.06	<10
18	<0.01	<0.01	0.05	<0.05	0.83	<0.5	0.45	<2
19	<0.01	<0.01	0.05	0.05	0.10	<0.5	<0.01	<1
20	0.05	0.01	0.07	0.05	24.5	<0.5	0.02	<1

TABLE 5. RAW WASTEWATER CHARACTERISTICS

Dyeing No. Substrate	1 Cotton	2 Polyamide	3 Polyester	4 Cotton	5 Cotton	6 Polyamide Carpet	7 Wool	8 Poly-	9 Polyester Carpet	10 Polyamide
Dye Class	Vat	1:2 Metal Complex	Disperse	After-copperable direct	Reactive	Disperse	Acid/ Chrome	Basic	Disperse	Acid
RAW WASTE CHARACTERISTICS										
ADMI Color	1910	370	315	525	3890	100	3200	5600	215	4000
Apparent ADMI Color[a]		---	---	1280	----	---	----	12,000	315	----
TOC, mg/l	265	400	300	135	150	130	210	255	240	315
BOD, mg/l	294	570	234	87	No response	78	135	210	159	240
pH	11.8	6.8	7.8	5.0	11.2	8.3	4.0	4.5	7.1	5.1
Cl^-, mg/l	190	neg.	33	520	9800	28	33	27	27	14
Susp. solids, mg/l	41	5	39	41	32	14	9	13	101	14
Total Dissol. Solids, mg/l	3945	1750	914	2763	12,500	396	1086	1469	771	2028
Total P, mg/l	----	----	---	19.6	4.9	7.2	4.7	5.4	0.7	<0.5
Kjeldahl N, mg/l	∿20	∿200	19.0	∿6	8.7	14.5	16.0	9.5	4.5	4.0
NH_3-N, mg/l	----	----	3.5	----	4.0	2.0	10.0	7.5	3.0	inter-fer.
NO_2/NO_3-N, mg/l	<1	<1.5	0.7	0.5	0.9	0.4	0.6	0.6	0.5	<0.3

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[a] Apparent ADMI Color Values were obtained by omitting the Celite filtration step from the published procedure.

TABLE 5. RAW WASTEWATER CHARACTERISTICS (continued)

Dyeing No. Substrate Dye Class	11 Rayon Direct	12 Rayon Direct Developed	13 Polyamide Carpet Disperse, Acid, Cationic	14 Polyester Disperse	15 Cotton Sulfur	16 Cotton Reactive	17 Polyester/ Cotton Disperse/Vat	18 Polyester Basic	19 Polyamide Carpet Disperse, Acid, Cationic	20 Cotton Naphthols
RAW WASTE CHARACTERISTICS										
ADMI Color	12,500	2730	210	1245	450	1390	365	1300	<50	2415
Apparent ADMI ADMI Color[a]	------	----	720	----	---	----	1100	2040	190	----
TOC, mg/l	140	55	130	360	400	230	350	1120	160	170
BOD, mg/l	15	12	42	198	990	102	360	1470	130	200
pH	6.6	3.2	6.7	10.2	3.7	9.1	10.1	5.0	6.5	9.3
Cl^-, mg/l	61	130	10	1680	42	57	167	17	22	7630
Susp. solids, mg/l	26	13	8	76	34	9	27	4	49	387
Total Dissol. Solids, mg/l	2669	918	450	1700	2000	691	2292	1360	258	10,900
Total P, mg/l	1.3	0.6	6.0	0.7	---	16.5	1.65	2.3	24.0	5.1
Kjeldahl N, mg/l	11.0	6.0	5.0	13.5	9.0	197.5	14.0	12.5	5.5	11.5
NH_3-N, mg/l	----	---	interfer.	interfer.	interfer.	10.0	12.0	3.5	<1.0	1.5
NO_2/NO_3-N,	1.75	16.5	0.5	0.3	2.6	0.5	0.9	<0.3	0.1	1.3

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[a] Apparent ADMI Color Values were obtained by omitting the Celite filtration step from the published ADMI procedure.

Benzidine analyses were carried out for only thirteen of the wastewaters and the values obtained were generally lower than 10 μg/l.

Color was measured according to the ADMI procedure.[2] Difficulties were encountered with color measurement of some dyeing wastewaters. For example, with some wastewaters the color was significantly reduced during the Celite filtration step of the color measurement procedure. On the other hand, turbidity in unfiltered samples interfered with color measurement. To obtain realistic color measurements of turbid dyeing wastewaters, dilutions were made. Dilution reduced the turbidity and enabled a more accurate determination of color in unfiltered samples. Throughout the study dilutions were made and the values compared with those of undiluted samples. Dilution proved a valid technique for arriving at apparent color values.

Wastewaters from dyeing of synthetic fibers with disperse dyes generally had lower color values (Table 5). Of these, wastewaters from carpet dyeing showed the least color. Since in some cases (nos. 4, 8, 13, 17, 18, 19) much of the color was removed in the filtration step, the color was also measured on unfiltered samples, usually by dilution. Color of dyeing wastewater no. 8 was measured after centrifugation.

Wastewaters generally exhibited low BOD (less than 400 mg/l) with the exception of no. 15 (sulfur on cotton, continuous procedure) and no. 18 (cationic on polyester by atmospheric exhaust procedure). For comparison, the BOD of domestic sewage is around 200-300 mg/l. Values for BOD could not be obtained for no. 5 since some component of this dyeing wastewater interfered with microbial activity.

With the exception of no. 18, TOC values were also low (less than 400 mg/l); that of domestic sewage is around 200-300 mg/l.

Suspended solids levels were generally low with the exception of no. 9 (disperse on polyester carpet by atmospheric exhaust procedure) and no. 20 (azoic on cotton by exhaust procedure).

In all cases, total phosphorus was less than 25 mg/l; for comparison, the total phosphorus in domestic sewage is in the range of 10-12 mg/l.

Total Kjeldahl nitrogen (organic + ammonia nitrogen) was likewise low (less than 20 mg/l) with the exception of no. 16 (reactive on cotton by continuous procedure, with urea addition) and no. 2 (1:2 metallized on polyamide by exhaust method, ammonium acetate addition). Domestic sewage concentrations are in the range of 25-50 mg/l.

High levels of chloride and total dissolved solids were found in no. 5 and no. 20.

Raw wastewater pH generally fell in the range of 4-8.5. Highly alkaline pH values (greater than 9.0) were found in wastewater nos. 1, 5, 14, 16, 17, and 20. With the exception of no. 14, these alkaline pH's were associated with cotton dyeings. Highly acid pH values (less than 4) were noted in nos. 12 and 15.

Overall, the wastewaters from the 20 dyeings showed much variation, as expected. In all cases, they were characterized by color and by organic content associated with substantial oxygen demand. The major goals of this project were directed toward removal of these two components.

References

1. EPA. Methods for Chemical Analysis of Water and Wastes. U. S. Environmental Protection Agency, Office of Technology Transfer, Washington, D.C. 1974.

2. Allen, W., R. E. Derby, C. E. Garland, J. M. Peret, W. B. Prescott, and M. Saltzman. Determination of Color of Water and Waste Water by Means of ADMI Color Values. In ADMI, Dyes and The Environment: Reports of Selected Dyes and Their Effects, Vol. I., American Dye Manufacturers Institute, Inc., N.Y. September 1973.

3. APHA, AWWA, WPCF. Standard Methods for the Examination of Water and Wastewater, 13th ed., American Public Health Association, N.Y. 1971.

4. FWPCA. FWPCA Methods for Chemical Analysis of Water and Wastes. U. S. Dept. of Interior, Federal Water Pollution Control Administration, Analytical Quality Control Laboratory, Cincinnati, Ohio. 1969.

SECTION VI

BIOLOGICAL TREATMENT

Biological treatability of 20 colored wastes from textile carpet dyeing operations was investigated in laboratory-scale studies. Many dyes resist biodegradation. Some, however, can be degraded biologically or can be removed from wastewaters by sorption onto biological floc. On the other hand, presence of some dyes, because of interference with the metabolism of organisms involved in oxidation of carbonaceous and nitrogenous compounds, may interfere with treatment of the non-colored waste components.[1]

Treatability of each wastewater was investigated in a series of experiments employing two-liter Erlenmeyer flasks. In each case, three sets of conditions were tested:

Set A - Dilutions of wastewater seeded with activated sludge from a bench-scale plant treating combined municipal and industrial wastewater from the City of Durham (dyeing wastewaters nos. 1-5) or municipal wastewater from the Town of Chapel Hill (dyeing wastewaters nos. 6-20), i.e., organisms not acclimated to the specific dyeing wastewater.

Set B - Dilutions seeded with microorganisms acclimated to the wastewater being tested (activated sludge from a pilot plant fed Durham or Chapel Hill wastewater supplemented with the dyeing wastewater).

Set C - Dilutions unseeded, but with Hg(II) added to prevent biological activity.

Sect C served as a control to distinguish between biological and nonbiological changes.

In each case, BOD nutrients[2] and yeast extract[3] were added to assure that nutrients and vitamins were not limiting. Initial pH was adjusted to pH 7.0. All sets were tested in duplicate. In each set, three wastewater dilutions were tested - 1, 10, and 100%. Each set was incubated on a shaker (80-90) rpm) in the dark at 20°C for 21 days. Initially and after incubation the samples were analyzed for soluble BOD, soluble TOC, color, and distribution of nitrogen species. In addition, for the 10% dilution the course of biological decomposition was monitored three times per week by removal of samples for TOC analysis. Figure 2 shows the experimental design.

Analyses were conducted according to the methods described in Table 3. In each case, soluble TOC and BOD were determined by filtering the sample through a glass fiber filter or a membrane filter (0.8 μm pore size) prior to analysis. Because solubilization of organics occurred in some cases, it was possible for soluble TOC to increase during the study. BOD determinations were not performed on samples from Set C because of the presence of mercury. Color analyses were conducted according to the ADMI procedure[4]. Nitrogen species were determined on an unfiltered sample. A detailed description of the procedures used in the biodegradability studies is given in the Appendix.

Results indicate that, in the majority of cases, biological treatment did not reduce color of dyebath wastewaters to levels which will be acceptable for discharge. On the other hand, in the majority of cases, presence of color did not interfere with BOD removal. In one case, however, the wastewater proved severely inhibitory to microbial activity and there was no removal of BOD; and in several cases, nitrification was inhibited. Effect of biological treatment on BOD, TOC, and color is shown in summary Tables 6, 7, and 8. Effect of wastes on nitrification is shown in summary Table 9. The course of TOC removal at the 10% dilution is shown graphically in Figures 3-22.

Results are presented for each dyeing wastewater in the following discussion.

Dyeing Wastewater No. 1. Vat Dyes on Cotton - Exhaust

Dyes: Vat Blue 18, Vat Black 13, Vat Orange 2; other components: Caustic soda, sodium hydrosulfite, acetic acid, surfactants, sodium perborate, tetrasodium pyrophosphate.

BOD removals of ≥ 97% were achieved in all dilutions in both acclimated and unacclimated cultures (Table 10). TOC removals were dependent on the dilution, with 100% removal at 1% dilution, over 80% removal at the 10% dilution, and 60-70% removal at 100%. Much greater removals were achieved in seeded than in unseeded samples. Color removal was dependent on dilution and type of culture. At the 10% dilution, 85% of the color was removed by acclimated seed, 68% by the unacclimated seed. Color removal was less than 20% at the 100% strength. There was some inhibition of nitrification

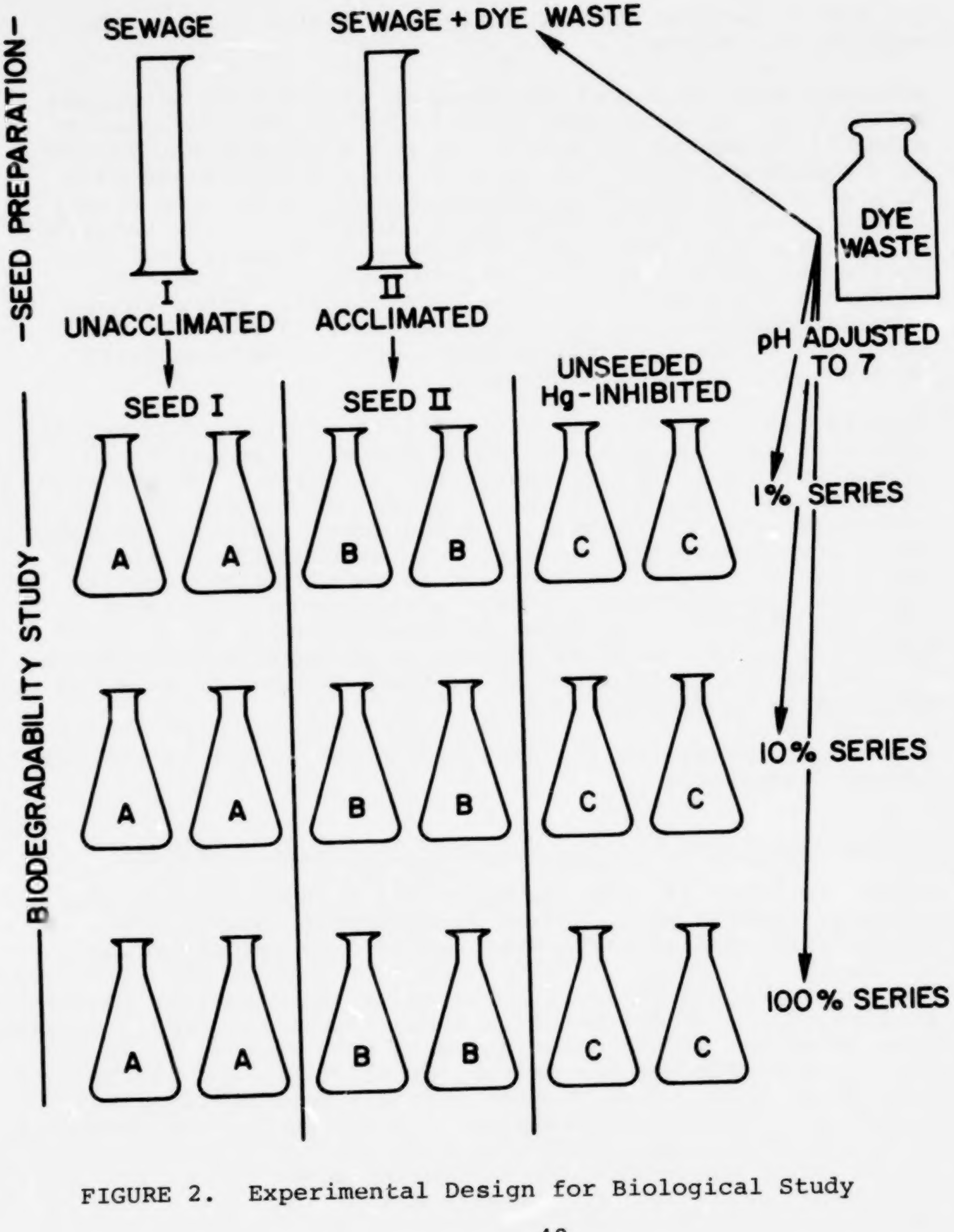
-SEED PREPARATION-
SEWAGE
SEWAGE + DYE WASTE
DYE WASTE
I
UNACCLIMATED
II
ACCLIMATED
pH ADJUSTED TO 7
SEED I
SEED II
UNSEEDED Hg-INHIBITED
-BIODEGRADABILITY STUDY-
A
B
C
1% SERIES
10% SERIES
100% SERIES

FIGURE 2. Experimental Design for Biological Study

TABLE 6. EFFECT OF BIOLOGICAL TREATMENT ON BOD, TOC, AND COLOR REMOVAL: 100% DILUTION

				TOC, mg/l		TOC	BOD_5, mg/l		BOD_5	Color, ADMI Units		
Dye Class	Substrate	Dye#	Set	Initial	Final	% Removal	Inital	Final	% Removal	Initial	Final	% Removal
Vat	Cotton	1	A-100	251	98	61	246	4	98	1,886	1,199	17
			B-100	249	73	71	222	1	100	1,080	937	13
			C-100	266	179	33	---	-	---	1,458	1,528	+5
Disperse	Polyester	3	A-100	276	163	41	288	<3	99	348	217	38
			B-100	289	183	37	294	3	99	255	246	4
			C-100	285	264	7	---	-	---	311	377	+21
Disperse	Polyamide Carpet	6	A-100	192	72	62	129	<1	>99	86	110	+28
			B-100	191	72	62	126	<1	>99	86	139	+62
			C-100	195	151	22	---	-	---	85	139	+64
Disperse	Polyester Carpet	9	A-100	280	115	59	234	<2	>99	333	262	21
			B-100	255	113	56	174	<2	>99	326	260	20
			C-100	250	168	33	---	-	---	334	353	+6
Disperse	Polyester	14	A-100	320	232	28	180	4	98	1,141	1,162	+2
			B-100	355	223	37	165	22	87	647	1,316	-
			C-100	445	268	40	---	--	--	1,072	1,165	+9
Vat & Disperse	Polyester-Cotton	17	A-100	289	85	70	>128	32	>75	371	302	18
			B-100	363	83	77	>128	38	>70	367	312	15
			C-100	327	372	+14	---	--	---	364	367	0
Sulfur	Cotton	15	A-100	510	52	90	810	<1	100	1,435	692	52
			B-100	460	54	88	870	<1	100	1,240	882	29
			C-100		98		---		---	1,345	1,090	19
Reactive	Cotton	5	A-100	184	117	36	---	--	---	4,084	3,991	2
			B-100	111	85	23	--- toxic	--	---			
			C-100	199	175	22	---	--	---	4,123	4,162	+1
Reactive	Cotton	16	A-100	118	24	80	118	1	99	719	690	4
			B-100	120	30	75	120	1	>99	730	712	2
			C-100	131	185	+41	---	--		727	724	<1

TABLE 6. EFFECT OF BIOLOGICAL TREATMENT ON BOD, TOC, AND COLOR REMOVAL: 100% DILUTION (continued)

				TOC, mg/l		TOC	BOD_5, mg/l		BOD_5	Color, ADMI Units		
Dye Class	Substrate	Dye#	Set	Initial	Final	% Removal	Initial	Final	% Removal	Initial	Final	% Removal
Basic	Polyacrylic	8	A-100	255	22	91	198	153[a]	23	11,260[a]	12,790[b]	----
			B-100	270	117	57	222	76	66	------	12,750[b]	None
			C-100	245	192	22	---	---	---	------	15,930[b]	----
Basic	Polyester	18	A-100	1150	346	70	1530	258	83	1,172	650	45
			B-100	1170	275	76	1620	216	87	1,304	670	50
			C-100	1020	1040	+2	----	---	---	1,059	1,050	0
Acid	Polyamide	10	A-100	280	211	25	270	<3	>99	3,300	3,110	6
			B-100	330	190	42	216	<3	>99	3,529	2,990	15
			C-100	305	305	0	---	---	---	2,970	2,925	2
Azoic	Cotton	20	A-100	174	58	67	204	3	99	2,850	509	82
			B-100	176	55	69	216	<1	100	2,805	497	82
			C-100	173	158	9	---	---	---	2,619	537	80
1:2 Metal Complex	Polyamide	2	A-100	492	123	67	530	5	99	300	297	1
			B-100	452	123	73	560	4	99	242	358	+48
			C-100	472	522	+10	---	---	---	261	281	+ 8
Direct (After-Copperable)	Cotton	4	A-100	143	27	81	132	5	96	577	623	+ 8
			B-100	139	27	81	108	6	94	564	716	+27
			C-100	134	145	+ 8	---	---	---	554	---	--
Direct	Rayon	11	A-100	170	153	10	51	<3	>94	12,750	11,350	11
			B-100	180	154	14	54	<3	>94	12,107	13,636	+13
			C-100	200	185	8	---	-	---	12,675	13,938	+10
Direct Developed	Rayon	12	A-100	66	45	32	42	<1	>98	3,190	2,455	23
			B-100	70	43	38	41	<1	>98	2,860	2,770	3
			C-100	68	--	--	---	---	--	2,950	2,860	3
Disperse + Acid + Cationic	Polyamide Carpet	13	A-100	115	53	54	90	11	88	637	210	67
			B-100	119	53	55	102	14	86	642	257	60
			C-100	121	77	36	---	---	---	653	410	37

[a] unfiltered
[b] centrifuged

TABLE 6. EFFECT OF BIOLOGICAL TREATMENT ON BOD, TOC, AND COLOR REMOVAL: 100% DILUTION (continued)

				TOC, mg/l		TOC	BOD_5, mg/l		BOD_5	Color, ADMI Units		
Dye Class	Substrate	Dye#	Set	Initial	Final	% Removal	Initial	Final	% Removal	Initial	Final	% Removal
Disperse + Acid + Cationic	Polyamide Carpet	19	A-100	150	34	77	129	2	98	28	---Too low to measure---	
			B-100	146	34	77	144	2	99	24		
			C-100	155	92	41	---	-	--	27		
Acid/Chrome	Wool	7	A-100	210	48	77	216	<1	>99		not measured, see 10 % dilution	
			B-100	245	34	86	216	<1	>99			
			C-100	200	204	+ 2	---	--	--			

Key: A - Unacclimated seed; B - Acclimated seed; C - Unseeded, $HgCl_2$ added

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TABLE 7. EFFECT OF BIOLOGICAL TREATMENT ON BOD, TOC, AND COLOR REMOVAL: 10% DILUTION

				TOC, mg/l		TOC	BOD_5, mg/l		BOD_5	Color, ADMI Units		
Dye Class	Substrate	Dye#	Set	Initial	Final	% Removal	Initial	Final	% Removal	Initial	Final	% Removal
Vat	Cotton	1	A-10	50	9	82	50	1	98	270	86	68
			B-10	45	7	84	50	<1	>98	252	38	85
			C-10	48	18	62	--	--	---	186	238	+28
Disperse	Polyester	3	A-10	49	16	67	76	1	99	94	52	45
			B-10	49	16	67	72	1	99	103	40	61
			C-10	45	65	+44	--	--	--	62	89	+44
Disperse	Polyamide Carpet	6	A-10	36	7	80	47	<1	>98	<1	Too low for analysis	
			B-10	38	9	76	50	<1	>98	8		
			C-10	37	37	0	--	--	--	--		
Disperse	Polyester Carpet	9	A-10	49	9	82	50	<1	>98	49	Too low for analysis	
			B-10	53	9	79	53	<1	>98	19		
			C-10	50	50	0	--	--	---	34		
Disperse	Polyester	14	A-10	50	25	50	34	<1	>97	160	150	6
			B-10	50	29	42	35	<1	>97	177	166	6
			C-10	49	42	9	--	--	---	169	200	+18
Vat & Disperse	Polyester-Cotton	17	A-10	63	14	78	>47	10	>78	92	62	33
			B-10	58	14	76	>51	7	>86	66	56	15
			C-10	67	59	12	--	--	--	52	66	+27
Sulfur	Cotton	15	A-10	68	5	93	114	<3	>97	164	33	80
			B-10	68	3	96	106	<3	>97	142	36	75
			C-10	--	67	0	---	--	--	93	42	55
Reactive	Cotton	5	A-10	39	18	54	---		--	541	530	2
			B-10	49	18	63	---	TOXIC	--	562		
			C-10	--	--	--	---		--	550	549	0
Reactive	Cotton	16	A-10	36	4	89	36	<1	>97	256	192	25
			B-10	35	4	88	35	<1	>97	282	195	31
			C-10	39	55	+41	---	--	--	191	172	10
Basic	Polyacrylic	8	A-10	41	10	73	55	3	94	1720 (unfiltered)	398*	77
			B-10	44	14	68	60	6	90		599*	65
			C-10	44	40	9	---	--	--		506*	70
Basic	Polyester	18	A-10	117	8	93	174	<1	>99	116	97	16
			B-10	127	12	90	204	<1	>99	155	146	6
			C-10	136	142	+7	---	--	--		125	
Acid	Polyamide	10	A-10	59	26	55	69	<1	>98	326	331	+2
			B-10	64	29	55	63	1	>98	350	355	+1
			C-10	62	60	3	---	--	--	320	315	2
Azoic	Cotton	20	A-10	52	6	88	59	1	>98	340	212	38
			B-10	47	8	83	44	<1	>98	297	229	23
			C-10	46	44	4	---	--	--	349	280	20
1:2 Metal Complex	Polyamide	2	A-10	65	16	77	39	4	90	187	40	79
			B-10	71	13	82	41	4	91	91	40	44
			C-10	65	74	+14	---	--	--	22	43	
Direct (After-Copperable)	Cotton	4	A-10	43	6	86	44	4	91	403	336	17
			B-10	40	6	85	41	4	90	420	306	27
			C-10	44	30	32	---	--	--	403	372	8
Direct	Rayon	11	A-10	40	11	72	42	<1	>98	1491	1003	33
			B-10	43	14	67	46	<1	>98	1508	1591	+6
			C-10	53	41	23	---	--	--	1395	1585	+14
Direct Developed	Rayon	12	A-10	25	2	92	35	<1	>97	306	182	40
			B-10	24	3	88	32	<1	>97	294	209	29
			C-10	25	22	12	---	--	--	295	163	45
Disperse + Acid + Cationic	Polyamide Carpet	13	A-10	31	4	87	35	3	91	107	36	66
			B-10	30	4	87	46	3	91	140	40	71
			C-10	26	22	15	---	--	---	97	39	60
Disperse + Acid + Cationic	Polyamide Carpet	19	A-10	27	[illegible]	100	30	<1	>97	[illegible]	Too low for analysis	
			B-10	27	[illegible]	96	29	<1	>97	12		
			C-10	26	22	15	---	--	---	14		
Acid/Chrome	Wool	7	A-10	47	6	87	52	<1	>98	117	147	+26
			B-10	46	6	87	44	<1	>98	105	167	+59
			C-10	47	42	11	---	--	---	93	148	+59

*centrifuged

Key: A - Unacclimated seed; B - Acclimated seed; C - Unseeded, $HgCl_2$ added

TABLE 8. EFFECT OF BIOLOGICAL TREATMENT ON BOD, TOC, AND COLOR REMOVAL: 1% DILUTION

				TOC, mg/l		TOC	BOD_5, mg/l		BOD_5	Color, ADMI Units		
Dye Class	Substrate	Dye #	Set[a]	Initial	Final	% Removal	Initial	Final	% Removal	Initial	Final	% Removal
Vat	Cotton	1	A-1	23	0	100	35	1	97	--	--	--
			B-1	27	0	100	37	1	97	--	--	--
			C-1	26	28	+3	--	--	--	--	--	--
Disperse	Polyester	3	A-1	22	0	100	44	1	98	40	14	65
			B-1	26	2	92	44	1	98	55	12	78
			C-1	26	31	+19	--	--	--	37	22	41
Disperse	Polyamide-Carpet	6	A-1	24	4	83	36	4	>97	--	--	--
			B-1	27	4	85	37	2	95	--	--	--
			C-1	25	24	4	--	--	--	--	--	--
Disperse	Polyester-Carpet	9	A-1	31	0	100	35	<1	97	--	--	--
			B-1	31	0	100	--	--	--	--	--	--
			C-1	29	26	10	--	--	--	--	--	--
Disperse	Polyester	14	A-1	16	2	88	17	1	94	--	--	--
			B-1	18	8	56	18	1	94	--	--	--
			C-1	17	13	24	--	--	--	--	--	--
Vat + Disperse	Polyester-Cotton	17	A-1	30	6	80	47	9	81	--	--	--
			B-1	27	6	78	40	10	75	--	--	--
			C-1	29	32	+10	--	--	--	--	--	--
Sulfur	Cotton	15	A-1	32	4	88	23	3	87	--	--	--
			B-1	32	2	94	25	3	88	--	--	--
			C-1	32	32	0	--	--	--	--	--	--
Reactive	Cotton	5	A-1	25	2	91	--	--	--	73	54	26
			B-1	31	8	74	--	--	--	121	72	40
			C-1	26	26	0	--	--	--	79	57	28

TABLE 8. EFFECT OF BIOLOGICAL TREATMENT ON BOD, TOC, AND COLOR REMOVAL: 1% DILUTION (continued)

Dye Class	Substrate	Dye #	Set	TOC, mg/1		TOC	BOD_5, mg/1		BOD_5	Color, ADMI Units		
				Initial	Final	% Removal	Initial	Final	% Removal	Initial	Final	% Removal
Direct Developed	Rayon	12	A-1	23	0	100	27	<1	96	84	26	70
			B-1	23	0	100	34	<1	97	71	26	63
			C-1	20	22	+10	--	--	--	80	44	45
Disperse + Acid + Basic	Polyamide Carpet	13	A-1	24	2	92	22	<1	>95	22	22	0
			B-1	19	2	89	23	<1	96	45	26	42
			C-1	19	22	+15	--	--	--	16	20	+25
Disperse + Acid + Basic	Polyamide Carpet	19	A-1	19	0	100	25	1	96	--	--	--
			B-1	19	0	100	19	<1	95	--	--	--
			C-1	20	12	40	--	--	--	--	--	--
Acid/Chrome	Wool	7	A-1	30	2	93	24	<1	96	--	--	--
			B-1	29	0	100	23	<1	96	--	--	--
			C-1	28	24	14	--	--	--	--	--	--

[a] In this table and in those following the number indicates the amount of wastewater in the test medium, i.e., A-1 refers to a 1% strength; A-10, to 10%, and A-100 to full-strength wastewater. A refers to test with unacclimated seed; B, to tests with acclimated seed; and C, to tests with unseeded medium with $HgCl_2$ addition.

TABLE 8. EFFECT OF BIOLOGICAL TREATMENT ON BOD, TOC, AND COLOR REMOVAL: 1% DILUTION (continued)

Dye Class	Substrate	Dye #	Set	TOC, mg/l Initial	TOC, mg/l Final	TOC % Removal	BOD_5, mg/l Initial	BOD_5, mg/l Final	BOD_5 % Removal	Color, ADMI Units Initial	Color, ADMI Units Final	Color, ADMI Units % Removal
Reactive	Cotton	16	A-1	20	0	100	20	<1	>95	--	--	--
			B-1	25	1	96	25	<1	>96	--	--	--
			C-1	23	24	+4	--	--	--	--	--	--
Basic	Polyacrylic	8	A-1	27	1	96	38	2	95	--	--	--
			B-1	26	9	65	26	2	92	--	--	--
			C-1	28	22	21	--	--	--	--	--	--
Basic	Polyester	18	A-1	34	2	94	42	4	98	--	--	--
			B-1	32	5	84	47	<1	98	--	--	--
			C-1	34	34	0	--	--	--	--	--	--
Acid	Polyamide	10	A-1	32	0	100	50	<1	>98	--	--	--
			B-1	34	2	94	41	1	98	--	--	--
			C-1	32	29	9	--	--	--	--	--	--
Azoic	Cotton	20	A-1	47	0	100	61	<1	>98	--	--	--
			B-1	43	2	95	34	<1	>97	--	--	--
			C-1	36	30	17	--	--	--	--	--	--
1:2 Metal Complex	Polyamide	2	A-1	23	0	100	20	3	85	64	22	--
			B-1	23	0	100	20	4	80	48	20	--
			C-1	23	24	4	--	--	--	26	8	--
Direct (After Copperable)	Cotton	4	A-1	24	0	100	29	2	93	52	14	73
			B-1	31	1	97	41	0	100	52	30	42
			C-1	29	20	31	--	--	--	57	32	47
Direct	Rayon	11	A-1	32	2	94	44	2	95	239	36	85
			B-1	30	1	97	48	<1	98	303	71	77
			C-1	39	26	33	--	--	--	221	78	65

TABLE 9. EFFECT OF DYEING WASTEWATERS ON NITRIFICATION

		10% Strength				100% Strength			
		TKN, mg/l		NO_2-N + NO_3-N, mg/l		TKN, mg/l		NO_2-N + NO_3-N, mg/l	
Dye #	Set	Initial	Final	Initial	Final	Initial	Final	Initial	Final
1	A	4.25	6.0	>0.3	2.1	23.0	26.0	0.5	0.5
	B		7.75		0.6		20.5	<0.3	<0.3
	C	3.6	7.5	<0.3	<0.5	30.0	----	0.7	0.9
2	A	24.0	15.0	0.6	12.2	203	----	1.3	---
	B	24.5	15.2	0.7	12.4	206	----	1.4	---
	C	25.5	26.5	<0.5	<0.3	231	----	1.1	1.1
3	A	7.0	7.75	>0.3	1.3	12.0	19.5	1.2	<0.3
	B	7.5	8.25	<0.3	<0.3	13.5	20.5	0.9	<0.3
	C		7.25	<0.3	<0.3	14.0	23.7	0.9	<0.3
4	A	4.5	5.5	<0.3	<0.3	9.5	11.0	0.6	<0.3
	B	4.5	5.75	<0.3	<0.3	10.0	12.0	0.6	<0.3
	C	4.0	3.0	<0.3	<0.3	10.0	10.5	0.5	0.6
5	A	6.5	<3.0	<0.3	6.0	14.2	16.2	1.0	0.7
	B	5.0	6.8	<0.3	0.8	14.5	16.0	0.9	0.6
	C	7.3	3.2	<0.3	<0.3	13.2	13.0	0.9	0.6
6	A	5.0	2.7	<0.3	6.4	18.0	6.0	0.5	10.6
	B	6.0	2.2	<0.3	6.2	19.0	6.0	0.4	10.8
	C	5.0	4.5	<0.3	<0.5	18.0	17.5	0.4	0.8
7	A	5.5	2.5	0.3	7.2	18.0	13.5	0.7	1.1
	B	5.5	7.8	0.2	1.0	19.5	15.0	0.6	0.8
	C	5.5	4.8	0.2	<0.3	17.5	10.2	0.6	0.8
8	A	4.0	5.5	<0.3	<0.5	17.5	11.0	0.3	0.9
	B	4.5	5.2	<0.3	<0.5	15.5	8.0	<0.3	0.8
	C	5.0	3.5	<0.3	<0.5	14.5	15.7	<0.3	1.6

TABLE 9. EFFECT OF DYEING WASTEWATERS ON NITRIFICATION (continued)

		10% Strength				100% Strength			
		TKN, mg/l		NO_2-N + NO_3-N, mg/l		TKN, mg/l		NO_2-N + NO_3-N, mg/l	
Dye #	Set	Initial	Final	Initial	Final	Initial	Final	Initial	Final
9	A	6.0	2.2	0.3	6.0	13.5	6.8	0.8	2.4
	B	7.5	2.2	0.3	6.2	13.5	6.2	0.7	3.1
	C	7.0	3.0	<0.3	<0.4	12.5	5.2	0.8	<0.3
10	A	5.0	7.5	<0.4	0.3	12.5	15.0	1.1	<0.4
	B	5.0	9.5	0.4	<0.7	----	13.8	0.95	<0.4
	C	4.5	4.5	<0.4	<0.3	11.5	12.5	0.7	<0.4
11	A	4.5	6.0	0.5	6.9	15.5	15.0	2.0	8.5
	B	7.5	5.0	0.5	5.8	17.0	14.5	2.0	8.2
	C	7.0	5.8	0.2	<0.7	15.0	17.3	2.7	2.8
12	A	5.5	2.5	---	6.8	----	----	---	---
	B	---	---	---	---	----	----	---	---
	C	---	---	---	---	----	----	---	---
13	A	3.0	2.2	<0.5	4.9	5.5	7.0	<0.95	<0.4
	B	3.5	2.2	<0.5	5.0	7.5	8.5	<0.95	2.0
	C	3.0	3.0	<0.5	<0.3	7.0	6.8	<0.95	0.75
14	A	4.5	3.2	<0.3	1.0	13.5	23.8	0.4	0.5
	B	3.0	4.0	<0.3	<0.5	13.5	28.0	0.6	<0.5
	C	3.0	2.2	<0.3	<0.4	13.5	23.5	<0.5	<0.6
15	A	5.5	3.0	<0.4	7.9	12.0	20.2	<0.4	<0.2
	B	5.0	4.5	<0.4	7.4	12.5	22.5	<0.4	1.3
	C	5.0	4.2	<0.4	<0.4	12.5	14.0	<0.4	2.3
16	A	19.5	8.5	0.95	15.0	127.5	41.5	3.6	60.5
	B	21.5	8.5	1.1	15.5	122.5	40.0	4.0	63.5
	C	20.5	21.5	<0.6	1.4	122.5	120.5	3.5	3.7
17	A	6.0	2.0	<0.3	6.7	20.0	15.2	1.11	0.35
	B	7.5	2.0	<0.3	6.9	22.0	19.2	1.19	0.27
	C	5.0	3.7	<0.2	<0.1	17.0	19.0	1.01	1.02
18	A	5.0	<2.0	<0.4	3.0	17.5	15.5	<0.4	<0.1
	B	5.0	2.0	<0.4	3.5	16.0	16.0	<0.4	<0.1
	C	5.5	4.0	<0.4	<0.1	15.5	17.0	<0.4	0.2

TABLE 9. EFFECT OF DYEING WASTEWATERS ON NITRIFICATION (continued)

		10% Strength				100% Strength			
		TKN, mg/l		NO_2-N + NO_3-N, mg/l		TKN, mg/l		NO_2-N + NO_3-N, mg/l	
Dye #	Set	Initial	Final	Initial	Final	Initial	Final	Initial	Final
19	A	2.5	2.0	0.3	3.2	10.0	5.0	0.2	0.3
	B	2.	2.0	0.1	3.6	9.5	7.5	0.2	1.1
	C	2.5	2.0	<0.1	<0.3	7.5	6.8	<0.1	<0.3
20	A	7.0	---	1.6	---	24.5	---	13.0	---
	B	7.5	---	1.7	---	31.5	---	13.0	---
	C	6.0	---	1.5	---	25.0	---	13.0	---

TABLE 10. BIOLOGICAL TREATABILITY OF WASTEWATER NO. 1

Set[a]	TOC			BOD_5			Color, ADMI Units		
	mg/l			mg/l					
	Initial	Final	% Removal	Initial	Final	% Removal	Initial	Final	% Removal
A-1	23	0	100	35	1	97	---	---	---
B-1	27	0	100	37	1	97	---	---	---
C-1	26	28	+8	--	--	--	---	---	---
A-10	50	9	82	50	1	98	270	86	68
B-10	45	7	84	50	<1	>98	252	38	85
C-10	48	18	62	--	--	---	186	238	+28
A-100	251	98	61	246	4	98	1,886	1,199	17
B-100	249	73	71	222	1	100	1,080	937	13
C-100	266	179	33	---	--	---	1,458	1,528	+5

TABLE 11. EFFECT OF WASTEWATER NO. 1 ON NITRIFICATION

Set	10% Strength				100% Strength			
	TKN, mg/l		NO_2-N + NO_3-N, mg/l		TKN, mg/l		NO_2-N + NO_3-N, mg/l	
	Initial	Final	Initial	Final	Initial	Final	Initial	Final
A	4.25	6.0	>0.3	2.1	23.0	26.0	0.5	0.5
B	---	7.75	---	0.6	---	20.5	<0.3	<0.3
C	3.6	7.5	<0.3	<0.5	30.0	---	0.7	0.9

[a] In this table and in those following the number indicates the amount of wastewater in the test medium, i.e., A-1 refers to a 1% strength; A-10, to 10%; and A-100 to full-strength wastewater.

in the 10% dilution and total inhibition at the 100% strength (Table 11).

Since some removal of TOC was obtained in the Hg-inhibited samples and since over the course of the experiment (Figure 3) TOC decreased in the 10% strength flask with mercury, evidently non-biological phenomena are responsible for part of the TOC removal.

Dyeing Wastewater No. 2. 1:2 Metal Complex Dye on Polyamide - Exhaust

Dyes: Acid Black 52; other components: Capracyl leveling salt (an ethylene oxide concentrate), ammonium acetate, sodium sulfate.

BOD removals of greater than 90% were achieved by both acclimated and unacclimated seed and at both 10% and 100% strengths (Table 12). Total removal of TOC was achieved in seeded flasks at 1%. At higher strengths, TOC removals were slightly better with acclimated seed and at the 10% dilution. Some color removal was achieved at the 10% dilution (79% by unacclimated, 44% by acclimated) but not at the 100% dilution. At the 10% level the wastewater did not affect nitrification (Table 13); nitrogen data were not available for the 100% strength.

As shown in Figure 4, over the course of the experiment the pattern of TOC removal was similar in the seeded flasks, whereas little or no reduction was achieved in the Hg-inhibited flasks, where in fact there was a slight increase in soluble TOC.

Dyeing Wastewater No. 3. Disperse Dyes on Polyester - Exhaust

Dyes: Disperse Blue 87, Disperse Yellow 42; other components: ethylene oxide condensate surfactant, complex diaryl sulfonate, ortho-phenylphenol carrier, acetic acid, soda ash, sodium hydrosulfite, anionic surfactant.

As shown in Table 14, BOD removals of ≥98% were achieved by both acclimated and unacclimated seed at all wastewater strengths. TOC removals occurred only in seeded flasks and were related to wastewater strength: ≥ 92% at 1% strength, 67% at 10% strength, ~40% at 100% strength. Additional confirmation of the association of TOC removal with seed is shown in Figure 5 which indicates TOC values over 21 days in the 10% dilutions. In fact, solubilization of TOC occur-

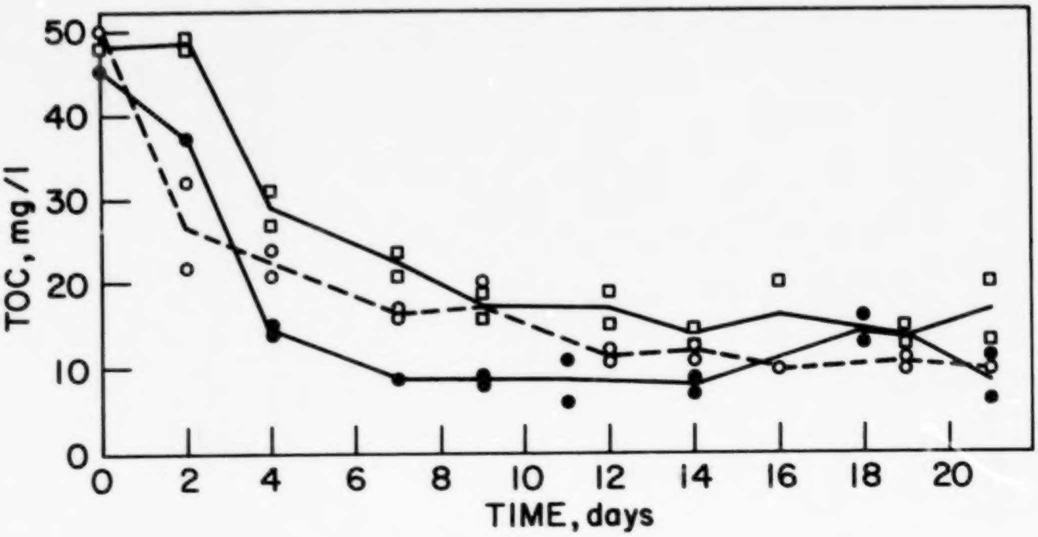

FIGURE 3. Dyeing Wastewater No. 1 (Vat Dyes on Cotton): Biodegradation. Unacclimated seed, o; acclimated seed, ●; unseeded, ◻.

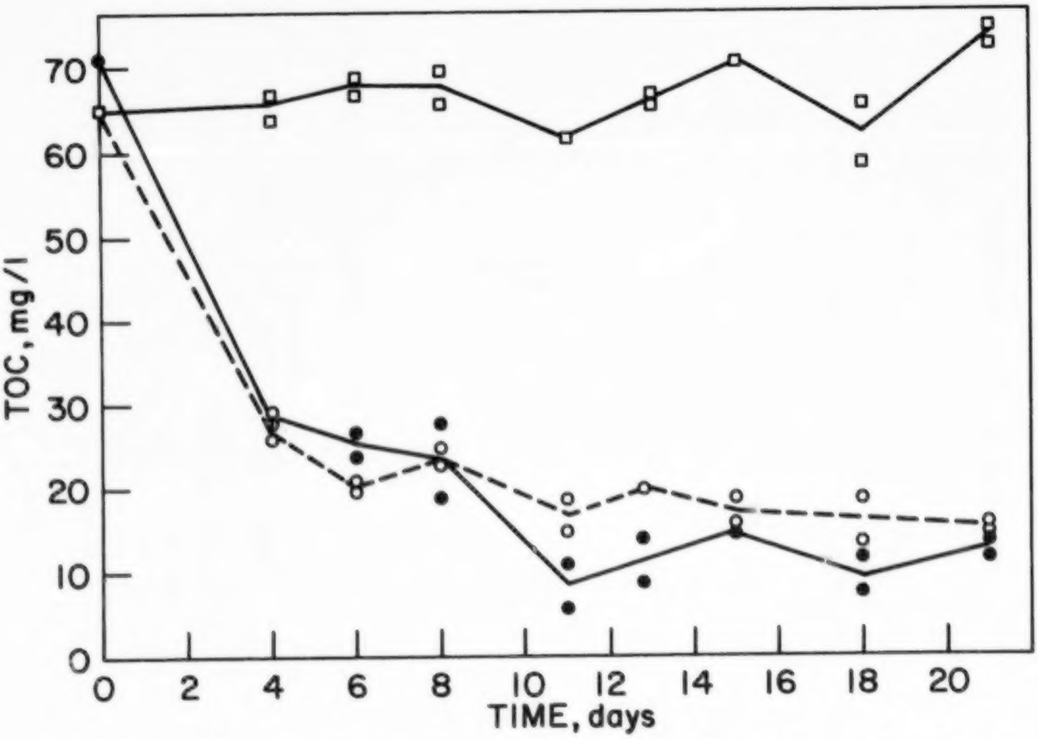

FIGURE 4. Dyeing Wastewater No. 2 (1:2 Metal Complex Dye on Polyamide): Biodegradation. Unacclimated seed, o; acclimated seed, ●; unseeded, ◻.

TABLE 12. BIOLOGICAL TREATABILITY OF WASTEWATER NO. 2

	TOC			BOD_5			Color, ADMI Units		
	mg/l			mg/l					
Set	Initial	Final	% Removal	Initial	Final	% Removal	Initial	Final	% Removal
A-1	23	0	100	20	3	85	64	22	66
B-1	23	0	100	20	4	80	48	20	58
C-1	23	24	4	--	--	--	26	8	69
A-10	65	16	77	39	4	90	187	40	79
B-10	71	13	82	41	4	91	91	40	44
C-10	65	74	+14	---	--	--	22	43	
A-100	492	123	67	530	5	99	300	297	1
B-100	452	123	73	560	4	99	242	358	+48
C-100	472	522	+10	---	--	--	261	281	+ 8

TABLE 13. EFFECT OF WASTEWATER NO. 2 ON NITRIFICATION

	10% Strength				100% Strength			
	TKN, mg/l		NO_2-N + NO_3-N, mg/l		TKN, mg/l		NO_2-N + NO_3-N, mg/l	
Set	Initial	Final	Initial	Final	Initial	Final	Initial	Final
A	24.0	15.0	0.6	12.2	203	---	1.3	---
B	24.0	15.2	0.7	12.4	206	---	1.4	---
C	25.5	26.5	<0.5	<0.3	231	---	1.1	1.1

TABLE 14. BIOLOGICAL TREATABILITY OF WASTEWATER NO. 3

	TOC			BOD_5			Color, ADMI Units		
	mg/l			mg/l					
Set	Initial	Final	% Removal	Initial	Final	% Removal	Initial	Final	% Removal
A-1	22	0	100	44	1	98	40	14	65
B-1	26	2	92	44	1	98	55	12	78
C-1	26	31	+19	--	-	--	37	22	41
A-10	49	16	67	76	1	99	94	52	45
B-10	49	16	67	72	1	99	103	40	61
C-10	45	65	+44	--	--	--	62	89	+44
A-100	276	163	41	288	<3	99	348	217	38
B-100	289	183	37	294	3	99	255	246	4
C-100	285	264	7	---	-	---	311	377	+21

TABLE 15. EFFECT OF WASTEWATER NO. 3 ON NITRIFICATION

	10% Strength				100% Strength			
	TKN, mg/l		NO_2-N + NO_3-N, mg/l		TKN, mg/l		NO_2-N + NO_3-N, mg/l	
Set	Initial	Final	Initial	Final	Initial	Final	Initial	Final
A	7.0	7.75	>0.3	1.3	12.0	19.5	1.2	<0.3
B	7.5	8.25	<0.3	<0.3	13.5	20.5	0.9	<0.3
C	---	7.25	<0.3	<0.3	14.0	23.7	0.9	<0.3

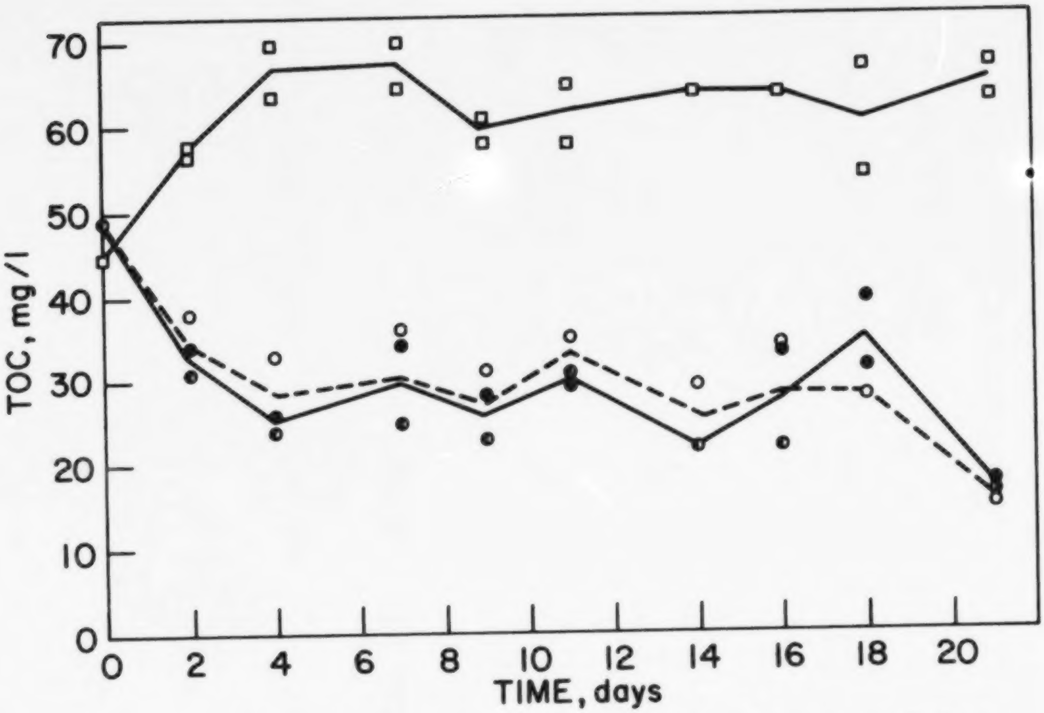

FIGURE 5. Dyeing Wastewater No. 3 (Disperse Dyes on Polyester): Biodegradation. Unacclimated seed, o; acclimated seed, ●; unseeded, ◻.

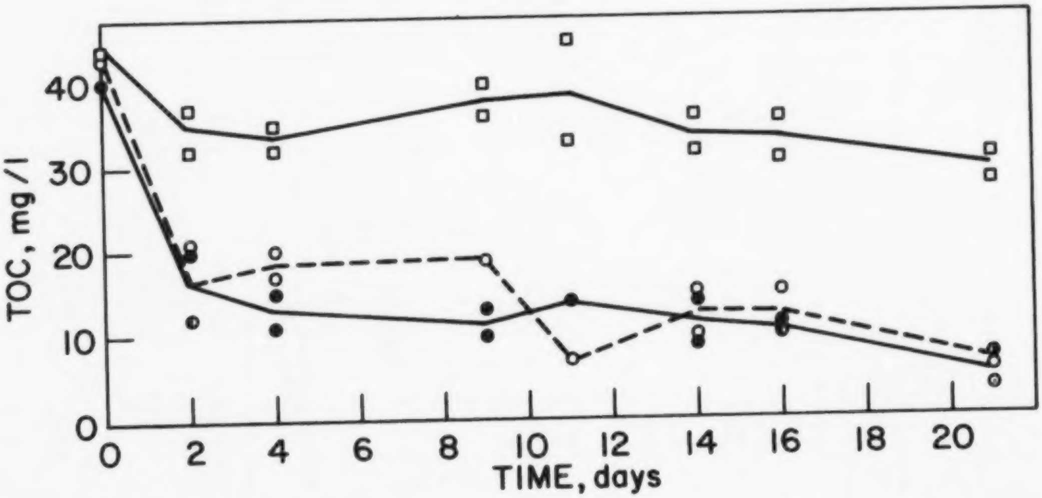

FIGURE 6. Dyeing Wastewater No. 4 (After-Copperable Direct Dye on Cotton): Biodegradation. Unacclimated seed, o; acclimated seed, ●; unseeded, ◻.

red in the unseeded flasks. Color removal was best with acclimated seed at 1% and at 10% strength. This dyeing wastewater was inhibitory to nitrification at both 10 and 100% strengths (Table 15).

Dyeing Wastewater No. 4. After-Copperable Direct Dye on Cotton - Exhaust

Dye: Direct Blue 160; other components: sodium metaphosphate, phosphated long-chain alcohols, soda ash, anionic surfactant, sequestrant, NaCl, acetic acid, copper sulfate.

Ninety percent or greater removals of BOD were achieved at 1%, 10%, and 100% strengths by both acclimated and unacclimated seed. TOC removals were unusually good: 81% at 100%, 85-86% at 10%. Only a small portion (<30%) of the TOC removal was due to nonbiological processes (Table 16). Further confirmation of this observation is shown in Figure 6. Color removals were extremely poor (<27%) and in some cases solubilization occurred, resulting in an increase in color as measured by the ADMI color test. This dyeing wastewater totally inhibited nitrification at both 10 and 100% strengths (Table 17).

Dyeing Wastewater No. 5. Reactive Dye on Cotton - Exhaust

Dye: Reactive Red 120; other components: anti-reducing agent, NaCl, soda ash, caustic soda, anionic surfactant.

Dyeing Wastewater No. 5 was the most inhibitory of the wastewaters studied. It inhibited oxidation of carbonaceous materials at 1%, 10%, and 100% strengths, even with "acclimated" seed. Nitrification was almost totally inhibited at the 10% and 100% strengths with the exception of the non-acclimated seed at 10% strength. At the 1% dilution TOC removals were good in seeded flasks (74%, 91%). At greater strengths TOC removals were poor: 54-63% in seeded flasks at 10% dyeing wastewater strength, 23-36% at 100% strength (Table 18). Figure 7 indicates that after 2-4 days there was little further removal of TOC. Color removal was nil at 10% and 100% dyeing wastewater strength and ≤40% at the 1% wastewater strength.

Nitrification occurred at 10% strength with unacclimated seed; no nitrification occurred at 10% strength in B or C flasks, or in any of those at 100% strength (Table 19).

TABLE 16. BIOLOGICAL TREATABILITY OF WASTEWATER NO. 4

	TOC			BOD$_5$			Color, ADMI Units		
	mg/l			mg/l					
Set	Initial	Final	% Removal	Initial	Final	% Removal	Initial	Final	% Removal
A-1	24	0	100	29	2	93	52	14	73
B-1	31	1	97	41	0	100	52	30	42
C-1	29	20	31	--	--	---	57	32	47
A-10	43	6	86	44	4	91	403	336	17
B-10	40	6	85	41	4	90	420	306	27
C-10	44	30	32	---	--	---	403	372	8
A-100	143	27	81	132	5	96	577	623	+3
B-100	139	27	81	108	6	94	564	716	+27
C-100	134	145	+8	---	--	---	554	---	--

TABLE 17. EFFECT OF WASTEWATER NO. 4 ON NITRIFICATION

	10% Strength				100% Strength			
	TKN, mg/l		NO_2-N + NO_3-N, mg/l		TKN, mg/l		NO_2-N + NO_3-N, mg/l	
Set	Initial	Final	Initial	Final	Initial	Final	Initial	Final
A	4.5	5.5	<0.3	<0.3	9.5	11.0	0.6	<0.3
B	4.5	5.75	<0.3	<0.3	10.0	12.0	0.6	<0.3
C	4.0	3.0	<0.3	<0.3	10.0	10.5	0.5	0.6

TABLE 18. BIOLOGICAL TREATABILITY OF WASTEWATER NO. 5

	TOC			BOD_5			Color, ADMI Units		
	mg/l			mg/l					
Set	Initial	Final	% Removal	Initial	Final	% Removal	Initial	Final	% Removal
A-1	25	2	91	---	---	---	73	54	26
B-1	31	8	74	---	---	---	121	72	40
C-1	26	26	0	---	---	---	79	57	28
A-10	39	18	54	---	---	---	541	530	2
B-10	49	18	63	---	inhibitory	---	562		
C-10	--			---	---	---	550	549	0
A-100	184	117	36	---	---	---	4,084	3,991	2
B-100	111	85	23	---	inhibitory	---			
C-100	199	175	22	---	---	---	4,123	4,162	+1

TABLE 19. EFFECT OF WASTEWATER NO. 5 ON NITRIFICATION

	10% Strength				100% Strength			
	TKN, mg/l		NO_2-N + NO_3-N, mg/l		TKN, mg/l		NO_2-N + NO_3-N, mg/l	
Set	Initial	Final	Initial	Final	Initial	Final	Initial	Final
A	6.5	3.0	0.3	6.0	14.2	16.2	1.0	0.7
B	5.0	6.8	0.3	0.8	14.5	16.0	0.9	0.6
C	7.3	3.2	0.3	0.3	13.2	13.0	0.9	0.6

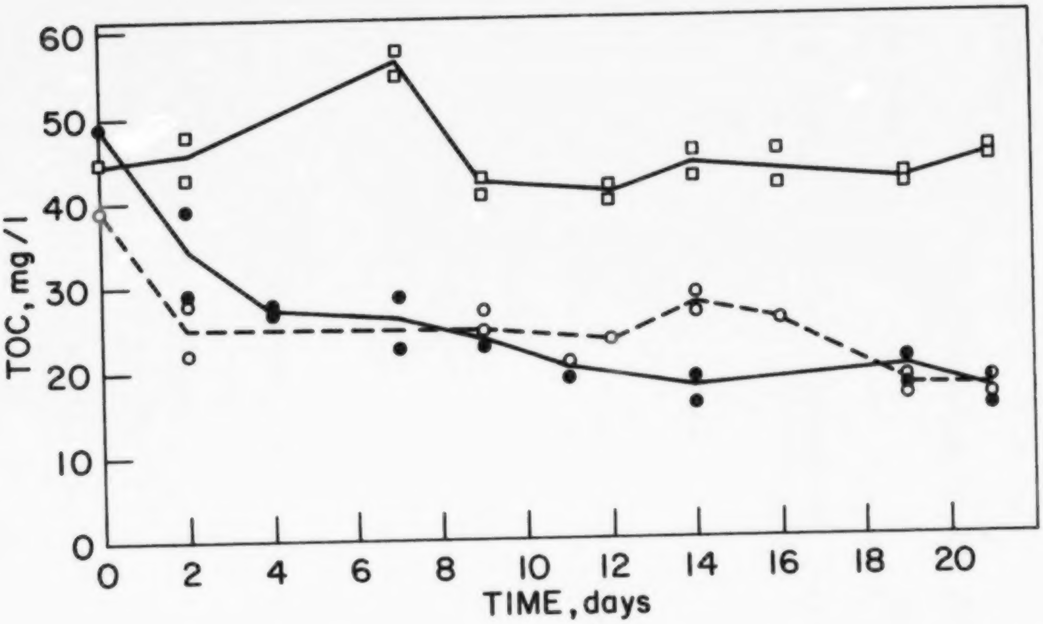

FIGURE 7. Dyeing Wastewater No. 5 (Reactive Dye on Cotton): Biodegradation. Unacclimated seed, o; acclimated seed, ●; unseeded, □.

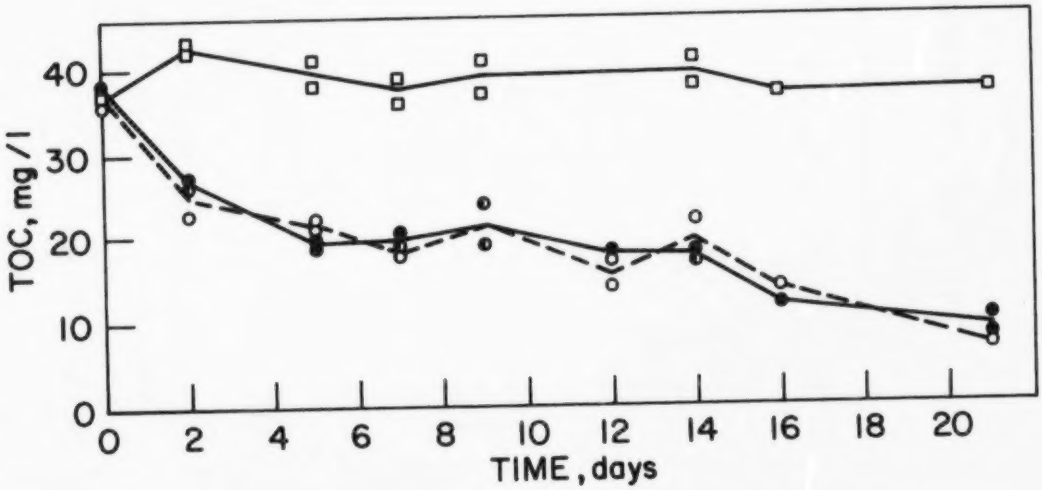

FIGURE 8. Dyeing Wastewater No. 6 (Disperse Dyes on Polyamide Carpet): Biodegradation. Unacclimated seed, o; acclimated seed, ●; unseeded, □.

Dyeing Wastewater No. 6. Disperse Dyes on Polyamide Carpet - Exhaust

Dyes: Disperse Yellow 3, Disperse Red 55, Disperse Violet 28; other components: anionic and nonionic surfactants, sequestrant, trisodium phosphate.

BOD removals of >95% were achieved with both acclimated and unacclimated seed at all strengths. TOC removals occurred in seeded flasks and were dependent on dilution: 83-85% at 1%, 76-80% at 10% strength, 62% at 100% strength. Association of TOC removal with biological activity is confirmed by TOC data over the 21-day period (Figure 8). Color levels were extremely low, even in the full strength waste. At full-strength there was no removal; on the contrary, soluble color increased (Table 20). There was no inhibition of nitrification even at full strength (Table 21).

Dyeing Wastewater No. 7. Acid Chrome Dye on Wool - Exhaust

Dye: Mordant Black 11; other components: acetic acid, anhydrous sodium sulfate, formic acid, sodium bichromate.

The BOD of Dyeing Wastewater No. 7 was easily removed, with ≥96% removal at all strengths and with both acclimated or unacclimated seed. TOC removals were associated with seeded flasks and related to wastewater concentration: 93-100% removal at 1% strength; 87% removal at the 10% strength, 77% removal by unacclimated seed at 100%, and 86% removal by acclimated seed at 100%. Association of TOC removal with biological activity is confirmed by Figure 9. In contrast, color removals were poor. Color tests performed on the samples at 10% strength indicated that soluble color actually increased during the incubation (Table 22). At 10% strength this waste had no effect on nitrification by unacclimated seed. A lesser degree of nitrification was obtained with acclimated seed at 10%. At full-strength little or no increase in oxidized nitrogen forms (nitrite + nitrate) was obtained (Table 23).

Dyeing Wastewater No. 8. Basic Dye on Polyacrylic - Exhaust

Dye: Basic Red 23; other components: organic cationic product as a retarder, sodium sulfate, acetic acid.

Dyeing Wastewater No. 8 was difficult to test due to its tendency to sorb onto solid surfaces. For example, it adhered to the Celite in the ADMI color test. BOD removals of 90-94% were achieved at the 1% and 10% strengths, but at

TABLE 20. BIOLOGICAL TREATABILITY OF WASTEWATER NO. 6

Set	TOC mg/l Initial	TOC mg/l Final	TOC % Removal	BOD_5 mg/l Initial	BOD_5 mg/l Final	BOD_5 % Removal	Color, ADMI Units Initial	Color, ADMI Units Final	Color, ADMI Units % Removal
A-1	24	4	83	36	4	>97	--	--	--
B-1	27	4	85	37	2	95	--	--	--
C-1	25	24	4	--	--	--	--	--	--
A-10	36	7	80	47	<1	>98	<1	Too low for analysis	
B-10	38	9	76	50	<1	>98	8		
C-10	37	37	0	--	--	--	--	--	--
A-100	192	72	62	129	<1	>99	86	110	+28
B-100	191	72	62	126	<1	>99	86	139	+62
C-100	195	151	22	---	--	--	85	139	+64

TABLE 21. EFFECT OF WASTEWATER NO. 6 ON NITRIFICATION

Set	10% Strength TKN, mg/l Initial	10% Strength TKN, mg/l Final	10% Strength NO_2-N + NO_3-N, mg/l Initial	10% Strength NO_2-N + NO_3-N, mg/l Final	100% Strength TKN, mg/l Initial	100% Strength TKN, mg/l Final	100% Strength NO_2-N + NO_3-N, mg/l Initial	100% Strength NO_2-N + NO_3-N, mg/l Final
A	5.0	2.7	<0.3	6.4	18.0	6.0	0.5	10.6
B	6.0	2.2	<0.3	6.2	19.0	6.0	0.4	10.8
C	5.0	4.5	<0.3	<0.5	18.0	17.5	0.4	0.8

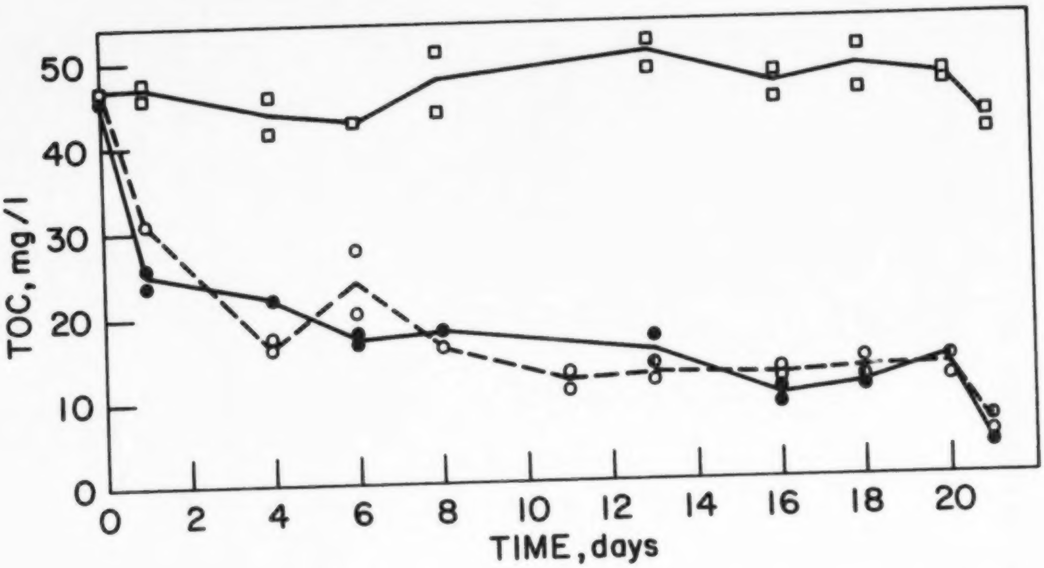

FIGURE 9. Dyeing Wastewater No. 7 (Acid-Chrome Dye on Wool): Biodegradation. Unacclimated seed, o; acclimated seed, ●; unseeded, ◻.

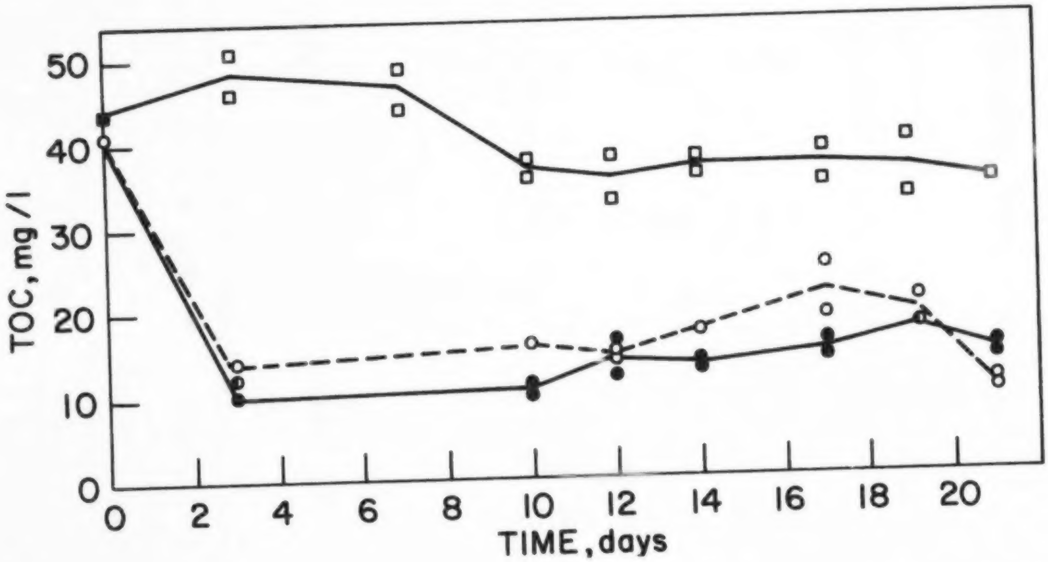

FIGURE 10. Dyeing Wastewater No. 8 (Basic Dye on Polyarylic): Biodegradation. Unacclimated seed, o; acclimated, ●; unseeded, ◻.

TABLE 22. BIOLOGICAL TREATABILITY OF WASTEWATER NO. 7

Set	TOC			BOD_5			Color, ADMI Units		
	mg/l			mg/l					
	Initial	Final	% Removal	Initial	Final	% Removal	Initial	Final	% Removal
A-1	30	2	93	24	<1	96	---	---	--
B-1	29	0	100	23	<1	96	---	---	--
C-1	28	24	14	--	--	--	---	---	--
A-10	47	6	87	52	<1	>98	117	147	+26
B-10	46	6	87	44	<1	>98	105	167	+59
C-10	47	42	11	--	--	--	93	148	+59
A-100	210	48	77	216	<1	>99	---	Not measured, see	
B-100	245	34	86	216	<1	>99	---	10% dilution	
C-100	200	204	+2	---	--	--	---	---	--

TABLE 23. EFFECT OF WASTEWATER NO. 7 ON NITRIFICATION

Set	10% Strength				100% Strength			
	TKN, mg/l		NO_2-N + NO_3-N, mg/l		TKN, mg/l		NO_2-N + NO_3-N, mg/l	
	Initial	Final	Initial	Final	Initial	Final	Initial	Final
A	5.5	2.5	0.3	7.2	18.0	13.5	0.7	1.1
B	5.5	7.8	0.2	1.0	19.5	15.0	0.6	0.8
C	5.5	4.8	0.2	<0.3	17.5	10.2	0.6	0.8

the 100% strength only 23% was removed by unacclimated seed and 66% by acclimated seed. TOC removals were erratic - around 70% at the 10% strength, 57% by acclimated seed at the 100% strength, and 91% removal by unacclimated seed at 100% strength. TOC removals were associated with presence of seed (Table 24 and Figure 10). Because of the tendency of the dye to sorb on Celite, color tests were performed on unfiltered or on uncentrifuged samples. This waste had an extremely high color - around 12,000 ADMI units at the 100% strength. Some color was removed at the 10% strength, evidently by non-biological processes, but residual colors were 400-600 units. No color was removed at the 100% strength. The waste interfered with nitrification at both the 10% and 100% strengths (Table 25).

Dyeing Wastewater No. 9. Disperse Dyes on Polyester Carpet - Exhaust

Dyes: Disperse Yellow 42, Disperse Blue 87; other components: dispersing agent, biphenyl carrier, antifoam agent, surfactants, sodium hydrosulfite, mono- and tri-sodium phosphate, acetic acid.

BOD removals of 97-99% were achieved at 1%, 10%, and at 100% strengths with both acclimated and unacclimated seed. TOC removal was dependent on concentration: 100% removal at 1% strength, around 80% at the 10% strength, around 60% at 100% strength. TOC removal was associated with presence of seed (Table 26 and Figure 11). Only 20% of the color was removed at the 100% strength; at 10% strength, the remaining color was too weak to measure accurately. At 10% strength, the waste did not affect nitrification, and only partial inhibition was noted at the 100% strength (Table 27).

Dyeing Wastewater No. 10. Acid Dye on Polyamide - Exhaust

Dye: Acid Blue 40; other components: anionic surfactant, Mesitol NBS (Verona), sodium sulfate, acetic acid.

BOD removals of ≥98% were achieved at all strengths. TOC removals varied with strength; they were associated with biological activity (Table 28 and Figure 12). At the 10% strength, ~55% of the TOC was removed by both unacclimated and acclimated seed. At 100% strength, 42% of the TOC was removed by acclimated seed; 25% by unacclimated seed. Initial color of the waste was high, ≅3000 ADMI units. No significant removals were obtained at either 10% or 100% strengths. This waste totally inhibited nitrification at both the 10% and 100% strengths (Table 29).

TABLE 24. BIOLOGICAL TREATABILITY OF WASTEWATER NO. 8

	TOC			BOD_6			Color, ADMI Units		
	mg/l			mg/l					
Set	Initial	Final	% Removal	Initial	Final	% Removal	Initial	Final	% Removal
A-1	27	1	96	38	2	95	----	---	---
B-1	26	9	65	26	2	92	----	---	---
C-1	28	22	21	--	--	--	----	---	---
A-10	41	10	73	55	3	94	----	398[b]	77
B-10	44	14	68	60	6	90	1720[a]	599[b]	65
C-10	44	40	9	--	--	--	----	506[b]	70
A-100	255	22	91	198	153[a]	23	11,260	12,790	---
B-100	270	117	57	222	76	66	----	12,750	None
C-100	245	192	22	---	---	--	----	15,930	---

TABLE 25. EFFECT OF WASTEWATER NO. 8 ON NITRIFICATION

	10% Strength				100% Strength			
	TKN, mg/l		NO_2-N + NO_3-N, mg/l		TKN, mg/l		NO_2-N + NO_3-N, mg/l	
Set	Initial	Final	Initial	Final	Initial	Final	Initial	Final
A	4.0	5.5	<0.3	<0.5	17.5	11.0	0.3	0.9
B	4.5	5.2	<0.3	<0.5	15.5	8.0	<0.3	0.8
C	5.0	3.5	<0.3	<0.5	14.5	15.7	<0.3	1.6

[a] unfiltered

[b] centrifuged

TABLE 26. BIOLOGICAL TREATABILITY OF WASTEWATER NO. 9

	TOC			BOD_5			Color, ADMI Units		
	mg/l			mg/l					
Set	Initial	Final	% Removal	Initial	Final	% Removal	Initial	Final	% Removal
A-1	31	0	100	35	<1	97	---	---	--
B-1	31	0	100	--	--	--	---	---	--
C-1	29	26	10	--	--	--	---	---	--
A-10	49	9	82	50	<1	>98	49	Too low for analysis	
B-10	53	9	79	53	<1	>98	19		
C-10	50	50	0	--	--	--	34	---	--
A-100	280	115	59	234	<2	>99	333	262	21
B-100	255	113	56	174	<2	>99	326	260	20
C-100	250	168	33	---	--	--	334	352	+6

TABLE 27. EFFECT OF WASTEWATER NO. 9 ON NITRIFICATION

	10% Strength				100% Strength			
	TKN, mg/l		NO_2-N + NO_3-N, mg/l		TKN, mg/l		NO_2-N + NO_3-N, mg/l	
Set	Initial	Final	Initial	Final	Initial	Final	Initial	Final
A	6.0	2.2	0.3	6.0	13.5	6.8	0.8	2.4
B	7.5	2.2	0.3	6.2	13.5	6.2	0.7	3.1
C	7.0	3.0	<0.3	<0.4	12.5	5.2	0.8	<0.3

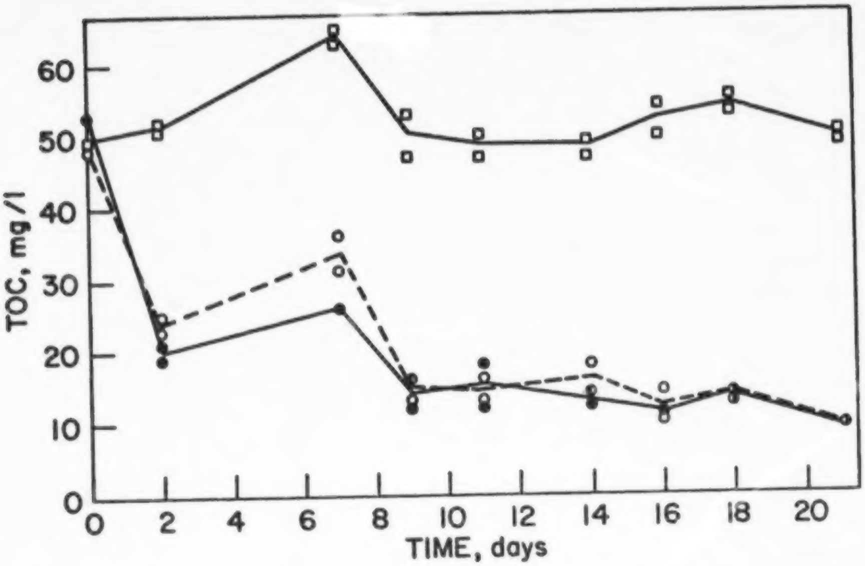

FIGURE 11. Dyeing Wastewater No. 9 (Disperse Dyes on Polyester Carpet): Biodegradation. Unacclimated seed, o; acclimated seed, ●; unseeded, □.

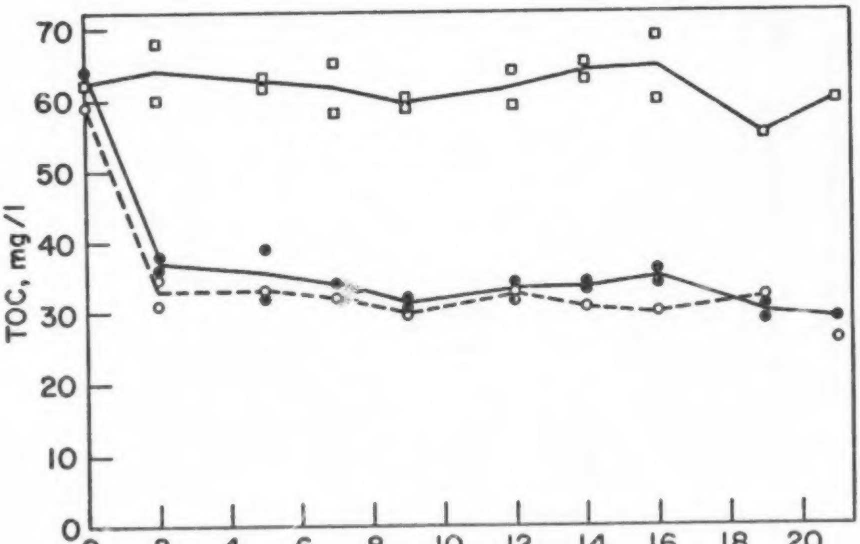

FIGURE 12. Dyeing Wastewater No. 10 (Acid Dye on Polyamide): Biodegradation. Unacclimated seed, o; acclimated seed, ●; unseeded, □.

TABLE 28. BIOLOGICAL TREATABILITY OF WASTEWATER NO. 10

	TOC			BOD_5			Color, ADMI Units		
	mg/l			mg/l					
Set	Initial	Final	% Removal	Initial	Final	% Removal	Initial	Final	% Removal
A-1	32	0	100	50	<1	>98	---	---	--
B-1	34	2	94	41	1	98	---	---	--
C-1	32	29	9	--	--	--	---	---	--
A-10	59	26	56	69	<1	>98	326	331	+2
B-10	64	29	55	63	<1	>98	350	355	+1
C-10	62	60	3	--	--	--	320	315	2
A-100	280	211	25	270	<3	>99	3,300	3,110	6
B-100	330	190	42	216	<3	>99	3,529	2,990	15
C-100	305	305	0	---	--	--	2,970	2,925	2

TABLE 29. EFFECT OF WASTEWATER NO. 10 ON NITRIFICATION

	10% Strength				100% Strength			
	TKN, mg/l		NO_2-N + NO_3-N, mg/l		TKN, mg/l		NO_2-N + NO_3-N, mg/l	
Set	Initial	Final	Initial	Final	Initial	Final	Initial	Final
A	5.0	7.5	<0.4	0.3	12.5	15.0	1.1	<0.4
B	5.0	9.5	0.4	<0.7	----	13.8	0.95	<0.4
C	4.5	4.5	<0.4	<0.3	11.5	12.5	0.7	<0.4

Dyeing Wastewater No. 11. Direct Dye on Rayon - Exhaust

Dye: Direct Black 38; other components: leveling agent, sodium sulfate.

BOD removals of >94% were achieved in all strengths by both acclimated and unacclimated seed. TOC removals were associated with biological activity (Table 30 and Figure 13) and were a function of waste strength: 94-97% at 1% strength, 70% removal at 10% strength, only 10-14% removal at 100% strength. Except at the 1% strength color removal was generally poor (<30%), the best being achieved by the unacclimated seed. In some flasks soluble color increased. Nitrification occurred in both 10% and 100% wastewater strengths (Table 31).

Dyeing Wastewater No. 12. Direct Developed Dye on Rayon

Dyes and other components: as for Dyeing Wastewater No. 11, with addition of the developer, 3-methyl-1-phenyl-5-pyrazolone, hydrochloric acid, sodium nitrite, and surfactant.

BOD removals of ≥96% were obtained at all dilutions. TOC removals were associated with biological activity (Table 32 and Figure 14) and were a function of wastewater strength: 100% removal at 1% strength, 88-92% removal at 10% strength, and 32-38% removal at 100% strength. The amount of TOC removed at all dilutions was about 20 mg/l and this may indicate that most of that removed was that contributed by the yeast extract. Color removal was a function of initial color level, with the best removals (63-70%) being obtained in the 1% strength. Substantial removal of color (45%) was achieved in unseeded flasks at the 1% and 10% strengths, suggesting that nonbiological processes were involved. Insufficient data were available on nitrogen forms, so effect on nitrification is unknown (Table 33).

Dyeing Wastewater No. 13. Disperse, Acid, and Basic Dyes on Polyamide Carpet

Dyes: Basic Red 73, Basic Blue 92, Disperse Yellow 3, Disperse Red 55, Disperse Blue 7, Acid Red 145, Acid Blue 122, Acid Yellow 198; other components: surfactants, mono- and tri-sodium phosphate, sequestrant.

BOD removals of ≥95% were achieved by both seeds at 1% waste strength; at 10% strength, 91%; at 100% strength, 86-88%. TOC removal was associated with presence of seed (Table 34 and Figure 15). Again, TOC removal was a function of dilution. TOC removals of 89-92% were achieved at 1% wastewater strength; at 10% strength, 87%; at 100% wastewater

TABLE 30. BIOLOGICAL TREATABILITY OF WASTEWATER NO. 11

	TOC			BOD_5			Color, ADMI Units		
	mg/l			mg/l					
Set	Initial	Final	% Removal	Initial	Final	% Removal	Initial	Final	% Removal
A-1	32	2	94	44	2	95	239	36	85
B-1	30	1	97	48	<1	98	303	71	77
C-1	39	26	33	--	--	--	221	78	65
A-10	40	11	72	42	<1	>98	1491	1003	33
B-10	43	14	67	46	<1	>98	1508	1591	+6
C-10	53	41	23	--	--	--	1395	1585	+14
A-100	170	153	10	51	<3	>94	12,750	11,350	11
B-100	180	154	14	54	<3	>94	12,107	13,636	+13
C-100	200	185	8	--	--	--	12,675	13,938	+10

TABLE 31. EFFECT OF WASTEWATER NO. 11 ON NITRIFICATION

	10% Strength				100% Strength			
	TKN, mg/l		NO_2-N + NO_3-N, mg/l		TKN, mg/l		NO_2-N + NO_3-N, mg/l	
Set	Initial	Final	Initial	Final	Initial	Final	Initial	Final
A	4.5	6.0	0.5	6.9	15.5	15.0	2.0	8.5
B	7.5	5.0	0.5	5.8	17.0	14.5	2.0	8.2
C	7.0	5.8	0.2	<0.7	15.0	17.3	2.7	2.8

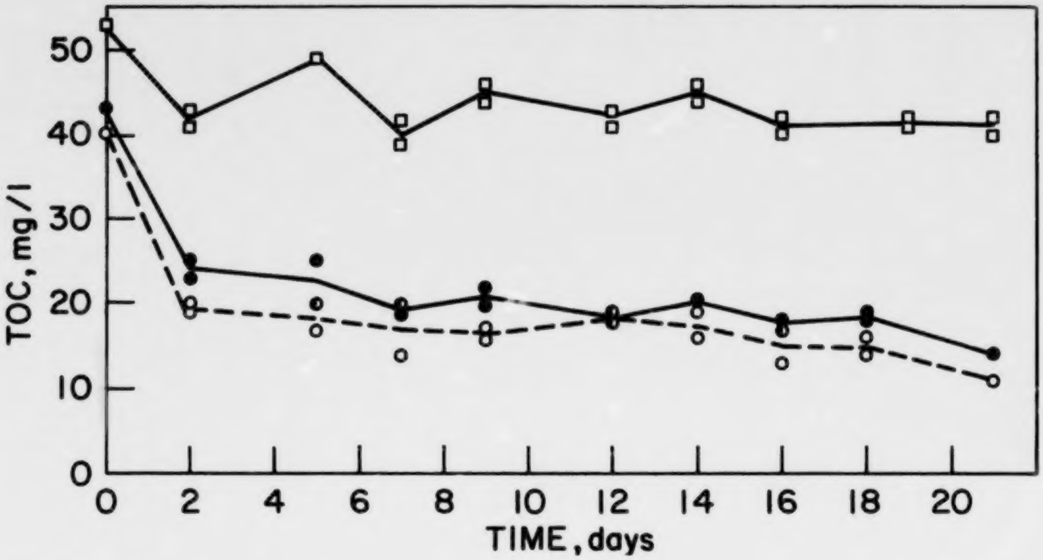

FIGURE 13. Dyeing Wastewater No. 11 (Direct Dye on Rayon): Biodegradation. Unacclimated seed, o; acclimated seed, ●; unseeded, □.

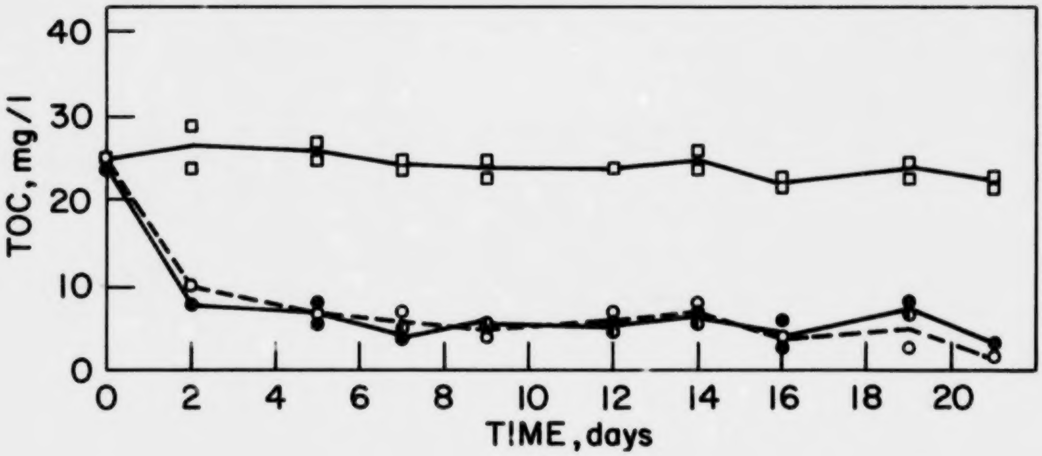

FIGURE 14. Dyeing Wastewater No. 12 (Direct Developed Dye on Rayon): Biodegradation. Unacclimated seed, o; acclimated seed, ●; unseeded, □.

TABLE 32. BIOLOGICAL TREATABILITY OF WASTEWATER NO. 12

	TOC			BOD_5			Color, ADMI Units		
	mg/l			mg/l					
Set	Initial	Final	% Removal	Initial	Final	% Removal	Initial	Final	% Removal
A-1	23	0	100	27	1	96	84	26	70
B-1	23	0	100	34	1	97	71	26	63
C-1	20	22	+10	--	--	--	80	44	45
A-10	25	2	92	35	1	97	306	182	40
B-10	24	3	88	32	1	97	294	209	29
C-10	25	22	12	--	--	--	295	163	45
A-100	66	45	32	42	1	98	3,190	2,455	23
B-100	70	43	38	41	1	98	2,860	2,770	3
C-100	68	--	--	--	--	--	-----	-----	3

TABLE 33. EFFECT OF WASTEWATER NO. 12 ON NITRIFICATION

	10% Strength				100% Strength			
	TKN, mg/l		NO_2-N + NO_3-N, mg/l		TKN, mg/l		NO_2-N + NO_3-N, mg/l	
Set	Initial	Final	Initial	Final	Initial	Final	Initial	Final
A	5.5	2.8	2.1	6.8	9.0	6.5	15.5	22.5
B	6.0	3.0	2.0	6.7	10.0	6.5	15.0	22.0
C	5.0	3.5	1.8	2.0	9.0	8.5	15.0	17.5

TABLE 34. BIOLOGICAL TREATABILITY OF WASTEWATER NO. 13

	TOC			BOD_5			Color, ADMI Units		
	mg/l			mg/l					
Set	Initial	Final	% Removal	Initial	Final	% Removal	Initial	Final	% Removal
A-1	24	2	92	22	<1	>95	22	22	0
B-1	19	2	89	23	<1	96	45	26	42
C-1	19	22	+15	--	--	--	16	20	+25
A-10	31	4	87	35	3	91	107	36	66
B-10	30	4	87	34	3	91	140	40	71
C-10	26	22	15	--	--	--	97	39	60
A-100	115	53	54	90	11	88	637	210	67
B-100	119	53	55	102	14	86	642	257	60
C-100	121	77	36	--	--	--	653	410	37

TABLE 35. EFFECT OF WASTEWATER NO. 13 ON NITRIFICATION

	10% Strength				100% Strength			
	TKN, mg/l		NO_2-N + NO_3-N, mg/l		TKN, mg/l		NO_2-N + NO_3-N, mg/l	
Set	Initial	Final	Initial	Final	Initial	Final	Initial	Final
A	3.0	2.2	<0.5	4.9	5.5	7.0	<0.95	<0.4
B	3.5	2.2	<0.5	5.0	7.5	8.5	<0.95	2.0
C	3.0	3.0	<0.5	<0.3	7.0	6.8	<0.95	0.75

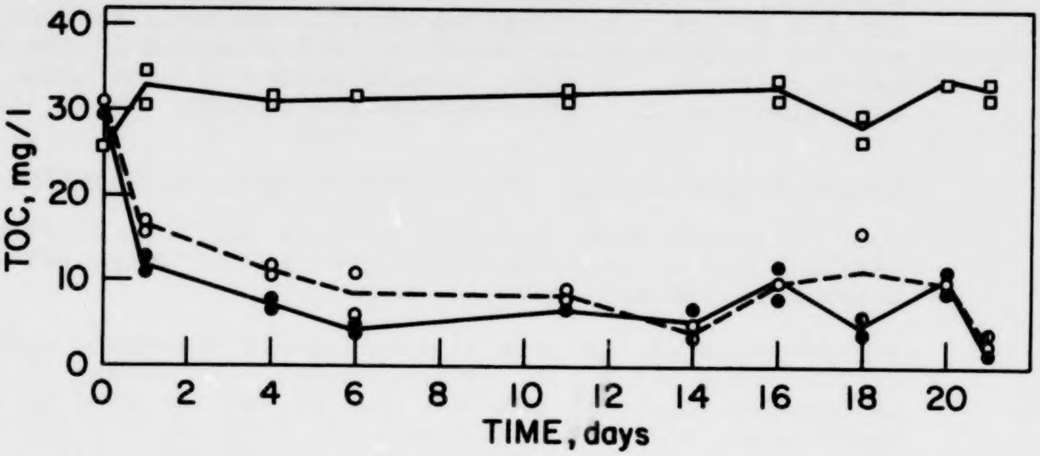

FIGURE 15. Dyeing Wastewater No. 13 (Disperse, Acid, and Cationic Dyes on Polyamide Carpet): Biodegradation. Unacclimated seed, o; acclimated seed, ●; unseeded, □.

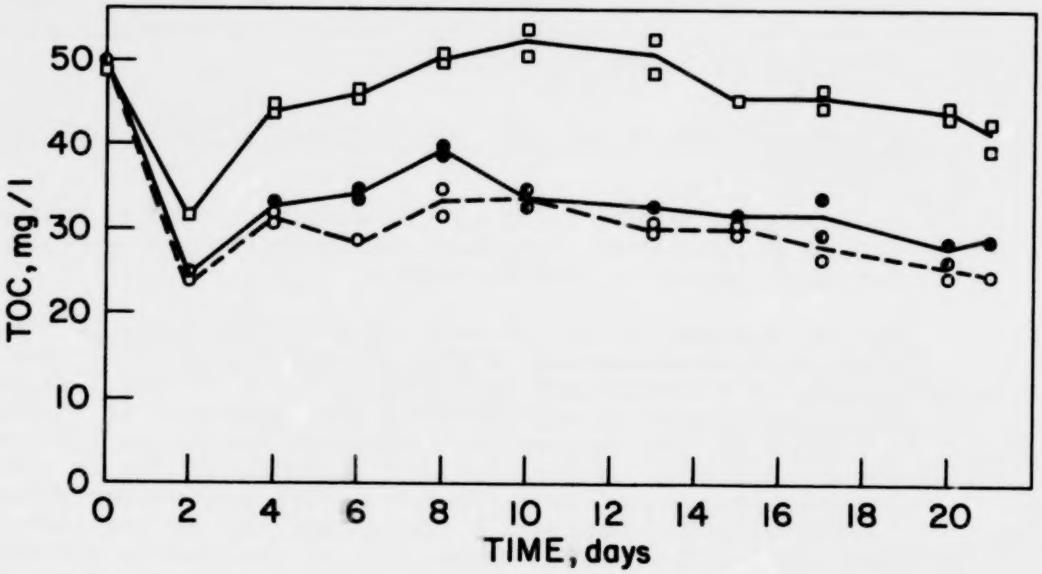

FIGURE 16. Dyeing Wastewater No. 14 (Disperse Dye on Polyester): Biodegradation. Unacclimated seed, o; acclimated seed, ●; unseeded, □.

strength, 54-55%. Despite the mix of dyes, the wastewater did not affect nitrification at 10% strength, and only partial inhibition was noted at full-strength in the acclimated cultures. However, nitrification did not occur at full-strength in the non-acclimated culture (Table 35).

Dyeing Wastewater No. 14. Disperse Dyes on Polyester

Dye: Disperse Blue 56; other components: trichlorbenzene carrier, acetic acid, sodium hydrosulfite, cetyl betaine, anionic surfactant, caustic soda.

BOD removals of 94% were achieved at 1% strength, and of greater than 97% at 10% strength with both seeds; at 100% wastewater strength, 98% BOD removal was achieved by unacclimated seed, 87% by acclimated seed. TOC removal was associated with presence of seed (Table 36 and Figure 16). At 10% strength, 42-50% removals were achieved. At 100% strength, unacclimated seed showed 28% removal; acclimated seed, 37% removal. At the 100% strength, the mercury-inhibited control experienced a 40% TOC removal, indicating that nonbiological processes were probably responsible for that removal. No color removal was achieved at either strength. Except with non-acclimated seed at 10% strength, Dyeing Wastewater No. 14 totally inhibited nitrification at both 10% and 100% strengths (Table 37).

Dyeing Wastewater No. 15. Sulfur Dye on Cotton, Continuous Process

Dye: Sulfur Black 1; other components: sodium sulfide and sodium polysulfide, alkylarylsulfonates blend surfactant, hydrogen peroxide, acetic acid.

Dyeing Wastewater No. 15 was readily treatable in comparison with other wastewaters (Table 38 and Figure 17). BOD removals of 97-100% were attained at both 10 and 100% wastewater strengths by both seeds. TOC removals of 93-96% were achieved at 10% wastewater strength; 88-90% at 100% wastewater strength. Color removals, partially due to nonbiological processes, were 75-80% at 10% wastewater strength; 29-52% at 100% strength. Unfortunately at the 100% strength the initial wastewater color was so intense (≅ 1300-1400 ADMI units) that even with the high percentage removals there were residual color levels of 700-900. While at the 10% wastewater strength nitrification was not affected, at 100% strength nitrification did not occur (Table 39).

TABLE 36. BIOLOGICAL TREATABILITY OF WASTEWATER NO. 14

	TOC			BOD_5			Color, ADMI Units		
	mg/l			mg/l					
Set	Initial	Final	% Removal	Initial	Final	% Removal	Initial	Final	% Removal
A-1	16	2	88	17	1	94	---	---	---
B-1	18	8	56	18	1	94	---	---	---
C-1	17	13	24	--	--	--	---	---	---
A-10	50	25	50	34	<1	>97	160	150	6
B-10	50	29	42	35	<1	>97	177	166	6
C-10	49	42	9	--	--	--	169	200	+18
A-100	320	232	28	180	4	98	1,141	1,162	+2
B-100	355	223	37	165	22	87	647	1,316	--
C-100	445	268	40	---	--	87	1,072	1,165	+9

TABLE 37. EFFECT OF WASTEWATER NO. 14 ON NITRIFICATION

	10% Strength				100% Strength			
	TKN, mg/l		NO_2-N + NO_3-N, mg/l		TKN, mg/l		NO_2-N + NO_3-N, mg/l	
Set	Initial	Final	Initial	Final	Initial	Final	Initial	Final
A	4.5	3.2	<0.3	1.0	13.5	23.8	0.4	0.5
B	3.0	4.0	<0.3	<0.5	13.5	28.0	0.6	<0.5
C	3.0	2.2	<0.3	<0.4	13.5	23.5	<0.5	<0.6

TABLE 38. BIOLOGICAL TREATABILITY OF WASTEWATER NO. 15

Set	TOC mg/l Initial	TOC mg/l Final	TOC % Removal	BOD_5 mg/l Initial	BOD_5 mg/l Final	BOD_5 % Removal	Color, ADMI Units Initial	Color, ADMI Units Final	Color, ADMI Units % Removal
A-1	32	4	88	23	3	87	---	---	---
B-1	32	2	94	25	3	88	---	---	---
C-1	32	32	0	--	--	--	---	---	---
A-10	68	5	93	114	<3	>97	164	33	80
B-10	68	3	96	106	<3	>97	142	36	75
C-10	--	67	0	---	--	--	93	42	55
A-100	510	52	90	810	<1	100	1,435	692	52
B-100	460	54	88	870	<1	100	1,240	882	29
C-100	---	98	--	---	--	---	1,345	1,090	19

TABLE 39. EFFECT OF WASTEWATER NO. 15 ON NITRIFICATION

Set	10% Strength TKN, mg/l Initial	10% Strength TKN, mg/l Final	10% Strength NO_2-N + NO_3-N, mg/l Initial	10% Strength NO_2-N + NO_3-N, mg/l Final	100% Strength TKN, mg/l Initial	100% Strength TKN, mg/l Final	100% Strength NO_2-N + NO_3-N, mg/l Initial	100% Strength NO_2-N + NO_3-N, mg/l Final
A	5.0	3.0	<0.4	7.9	12.0	20.2	<0.4	<0.2
B	5.0	4.5	<0.4	7.4	12.5	22.5	<0.4	1.3
C	5.0	4.2	<0.4	<0.4	12.5	14.0	<0.4	2.3

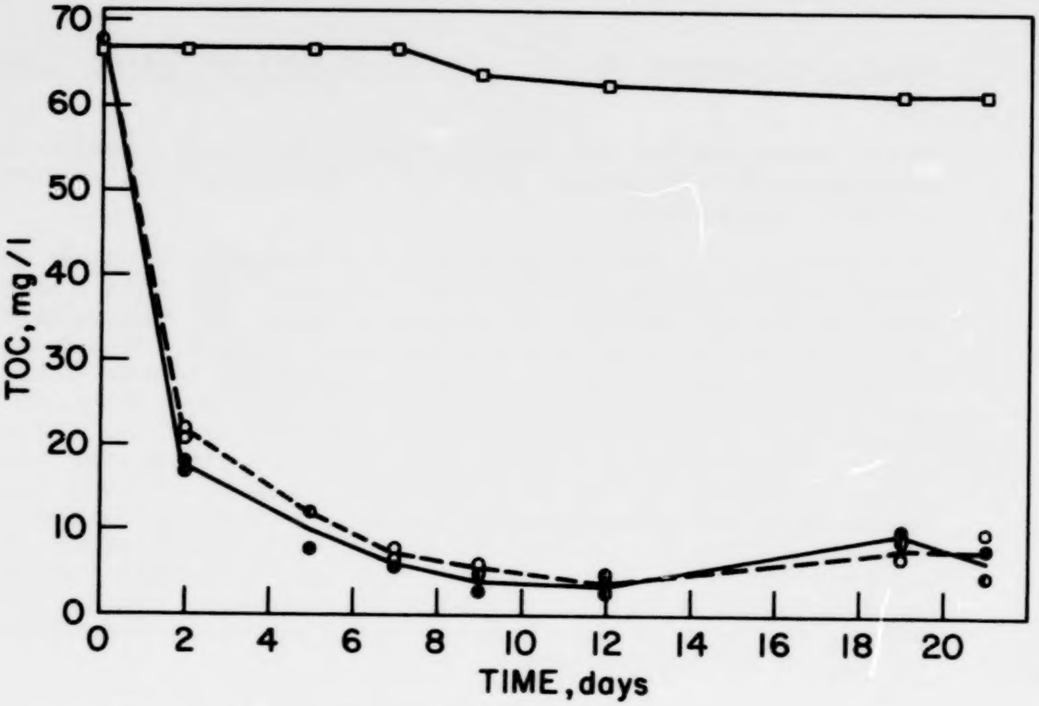

FIGURE 17. Dyeing Wastewater No. 15 (Sulfur Dye on Cotton): Biodegradation. Unacclimated seed, o; acclimated seed, ●; unseeded, □.

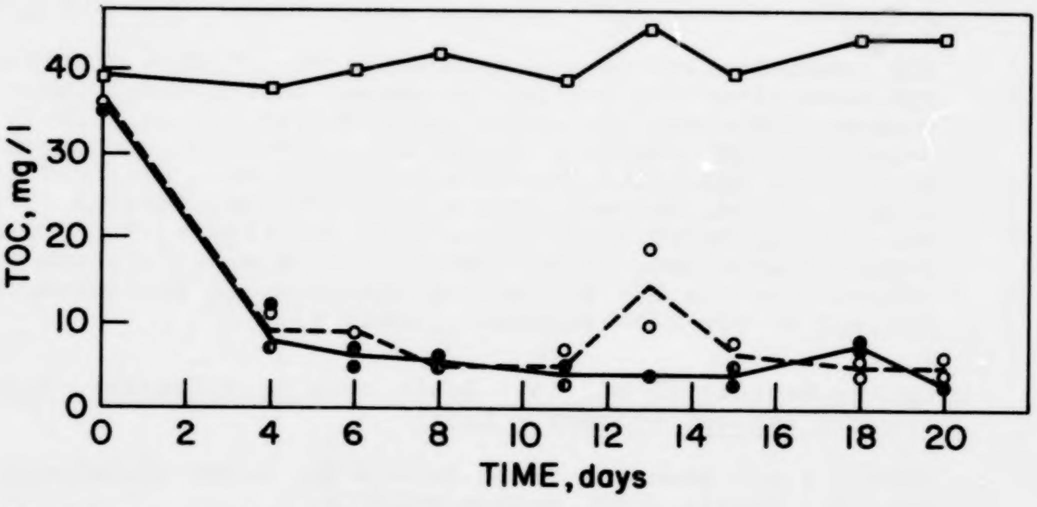

FIGURE 18. Dyeing Wastewater No. 16 (Reactive Dye on Cotton): Biodegradation. Unacclimated seed, o; acclimated seed, ●; unseeded, □.

Dyeing Wastewater No. 16. Reactive Dyes on Cotton - Continuous

Dye: Reactive Red 40; other components: urea, sodium m-nitrobenzene-sulfonate, soda ash, natural gum thickener, anionic surfactant.

BOD removals of 95% or greater were achieved by both acclimated and unacclimated seeds at 1%, 10%, and 100% dyeing wastewater strengths. In seeded flasks, TOC removals of 88-89% were achieved at 10% wastewater strength, 75-80% at 100% strength. Removal occurred only in seeded flasks (Table 40 and Figure 18). In contrast, in the mercury-inhibited flasks TOC increased probably by solubilization. In all cases, color removals were poor. At 10% wastewater strength color decreased by 25-31% in seeded flasks; at 100% wastewater strength, essentially no color removal occurred. Dyeing Wastewater No. 16 had no effect on nitrification, even at 100% strength. The initial Kjeldahl nitrogen values were unusually high ($\cong$ 125 mg N/l), probably due to the urea. During the test period much of the Kjeldahl N was converted to NO_2^--N and NO_3^--N (Table 41).

Dyeing Wastewater No. 17. Vat and Disperse Dyes on 50/50 Cotton-Polyester Blend, Continuous Dyeing, Thermosol-Pad-Steam Process

Dyes: Vat Black 25, Vat Green 8, Vat Green 3, Disperse Blue 62, Disperse Orange 41, Disperse Brown 2; other components: natural gums solution, sodium alkylaryl sulfonate, hydrogen peroxide, acetic acid, caustic soda, sodium hydrosulfite.

BOD removals with Dyeing Wastewater No. 17 were difficult to estimate since the initial strengths were underestimated. However, since the raw waste had a BOD of 360 mg/l it is estimated that BOD removals at the 100% wastewater strength were about 90%. TOC removals of 70-80% were achieved in seeded flasks, whereas little or no TOC was removed in the mercury-inhibited flasks (Table 42 and Figure 19). Color removals were poor in all cases. While nitrification was not affected at the 10% wastewater strength, it was strongly inhibited at the 100% strength (Table 43).

Dyeing Wastewater No. 18. Basic Dyes on Polyester, Atmospheric Exhaust Process - Batch

Dyes: Basic Blue 41, Basic Yellow 11; other components: carrier, acetic acid, sodium sulfate.

TABLE 40. BIOLOGICAL TREATABILITY OF WASTEWATER NO. 16

Set	TOC			BOD_5			Color, ADMI Units		
	mg/l			mg/l					
	Initial	Final	% Removal	Initial	Final	% Removal	Initial	Final	% Removal
A-1	20	0	100	20	<1	>95	---	---	---
B-1	25	1	96	25	<1	>96	---	---	---
C-1	23	24	+4	--	--	--	---	---	---
A-10	36	4	89	36	<1	>97	256	192	25
B-10	35	4	88	35	<1	>97	282	195	31
C-10	39	55	+41	--	--	--	191	172	10
A-100	118	24	80	118	1	99	719	690	4
B-100	120	30	75	120	1	>99	730	712	2
C-100	131	185	+41	---	--	--	727	724	<1

TABLE 41. EFFECT OF WASTEWATER NO. 16 ON NITRIFICATION

Set	10% Strength				100% Strength			
	TKN, mg/l		NO_2-N + NO_3-N, mg/l		TKN, mg/l		NO_2-N + NO_3-N, mg/l	
	Initial	Final	Initial	Final	Initial	Final	Initial	Final
A	19.5	8.5	0.95	15.0	127.5	41.5	3.6	60.5
B	21.5	8.5	1.1	15.5	122.5	40.0	4.0	63.5
C	20.5	21.5	<0.6	1.4	122.5	120.5	3.5	3.7

TABLE 42. BIOLOGICAL TREATABILITY OF WASTEWATER NO. 17

	TOC			BOD_5			Color, ADMI Units		
	mg/l			mg/l					
Set	Initial	Final	% Removal	Initial	Final	% Removal	Initial	Final	% Removal
A-1	30	6	80	47	9	81	---	---	---
B-1	27	6	78	40	10	75	---	---	---
C-1	29	32	+10	--	--	--	---	---	---
A-10	63	14	78	>47	10	>78	92	62	33
B-10	58	14	76	>51	7	>86	66	56	15
C-10	67	59	12	--	--	--	52	66	+27
A-100	289	85	70	>128	32	>75	371	302	18
B-100	363	83	77	>128	38	>70	367	312	15
C-100	327	372	+14	---	--	--	364	367	0

TABLE 43. EFFECT OF WASTEWATER NO. 17 ON NITRIFICATION

	10% Strength				100% Strength			
	TKN, mg/l		NO_2-N + NO_3-N, mg/l		TKN, mg/l		NO_2-N + NO_3-N, mg/l	
Set	Initial	Final	Initial	Final	Initial	Final	Initial	Final
A	6.0	2.0	<0.3	6.7	20.0	15.2	1.11	0.35
B	7.5	2.0	<0.3	6.9	22.0	19.2	1.19	0.27
C	5.0	3.7	<0.2	<0.1	17.0	19.0	1.01	1.02

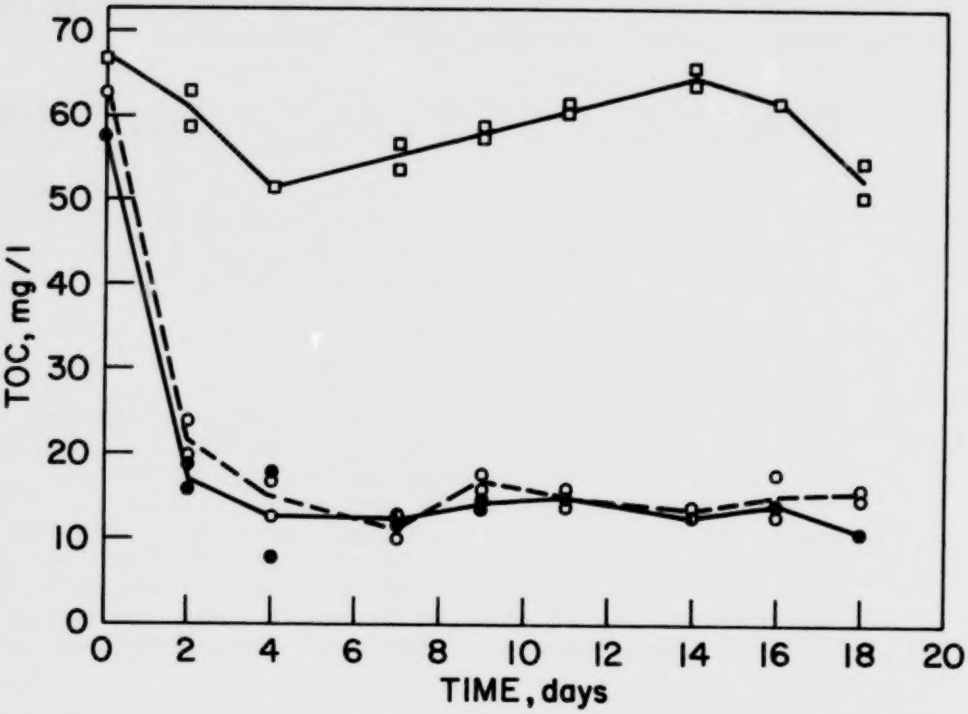

FIGURE 19. Dyeing Wastewater No. 17 (Disperse and Vat Dyes on Polyester/Cotton): Biodegradation. Unacclimated seed, o; acclimated seed, ●; unseeded, □.

BOD removals in Dyeing Wastewater No. 18 were dependent on wastewater strength. At the 1% and 10% strengths, ≥98% of the BOD was removed, whereas at 100% strength only 83-87% removals were achieved. TOC removals, likewise, were dependent on wastewater strength. In seeded flasks, 90-93% removals were obtained at 10%; at 100% strength, 70-76%. TOC removals were achieved only in seeded flasks (Table 44 and Figure 20). In mercury-inhibited flasks, no TOC was removed. In seeded flasks color removals were very poor at 10% dye strength, but 45-50% at full strength; the reason for this is unknown. No color removal occurred in unseeded flasks. Nitrification occurred at 10% strength but not at 100% strength (Table 45).

Dyeing Wastewater No. 19. Disperse, Acid, and Basic Dyes on Polyamide Carpet, Kuster Simulation Process - Continuous

Dyes: Basic Yellow 31, Acid Blue 298, Acid Red (Stylacyl Red RB), Disperse Blue 7; other components: ethylene oxide condensates, acetic acid or monosodium phosphate (for pH adjustment), anionic surfactant, natural gum thickener.

BOD removals of ≥95% were achieved in all seeded dilutions. TOC removals were unusually good (≥77%) and were associated with biological activity (Table 46 and Figure 21). At the 10% dilution, seeded flasks achieved 96-100% TOC removals, whereas in the unseeded flasks only 15% was removed. At 100% strength, the unacclimated seed removed 77% of the TOC; the acclimated seed, 86%. In contrast, little or no TOC was removed in the mercury-inhibited controls. The color levels of Dyeing Wastewater No. 19 were so low that accurate estimates of color could not be obtained. Nitrification was not unaffected at the 10% strength, but was markedly inhibited in the presence of the full-strength wastewater (Table 47).

Dyeing Wastewater No. 20. Naphthol on Cotton - Exhaust Procedure

Dyes: Azoic Coupling Compound 7, Azoic Diazo Component 13; other components: acetic acid, caustic soda, soda ash, Calgon, common salt.

In seeded flasks BOD removals of ≥98% were achieved. TOC removals were also good and were associated only with seeded flasks (Table 48 and Figure 22). At the 10% dyeing wastewater strength, seeded flasks removed 83-88% of the TOC; at 100% wastewater strength, 67-69% TOC removals were experienced. Color removals were much better at 100% strength

TABLE 44. BIOLOGICAL TREATABILITY OF WASTEWATER NO. 18

	TOC			BOD_5			Color, ADMI Units		
	mg/l			mg/l					
Set	Initial	Final	% Removal	Initial	Final	% Removal	Initial	Final	% Removal
A-1	34	2	94	42	4	98	---	---	---
B-1	32	5	84	47	<1	98	---	---	---
C-1	34	34	0	--	--	--	---	---	---
A-10	117	8	93	174	<1	>99	116	97	16
B-10	127	12	90	204	<1	>99	155	146	6
C-10	136	142	+7	---	--	--	---	125	---
A-100	1150	346	70	1530	258	83	1,172	650	45
B-100	1170	275	76	1620	216	87	1,304	670	50
C-100	1020	1040	+2	----	---	--	1,059	1,050	0

TABLE 45. EFFECT OF WASTEWATER NO. 18 ON NITRIFICATION

	10% Strength				100% Strength			
	TKN, mg/l		NO_2-N + NO_3-N, mg/l		TKN, mg/l		NO_2-N + NO_3-N, mg/l	
Set	Initial	Final	Initial	Final	Initial	Final	Initial	Final
A	5.0	<2.0	<0.4	3.0	17.5	15.5	<0.4	<0.1
B	5.0	2.0	<0.4	3.5	16.0	16.0	<0.4	<0.1
C	5.5	4.0	<0.4	<0.1	15.5	17.0	<0.4	0.2

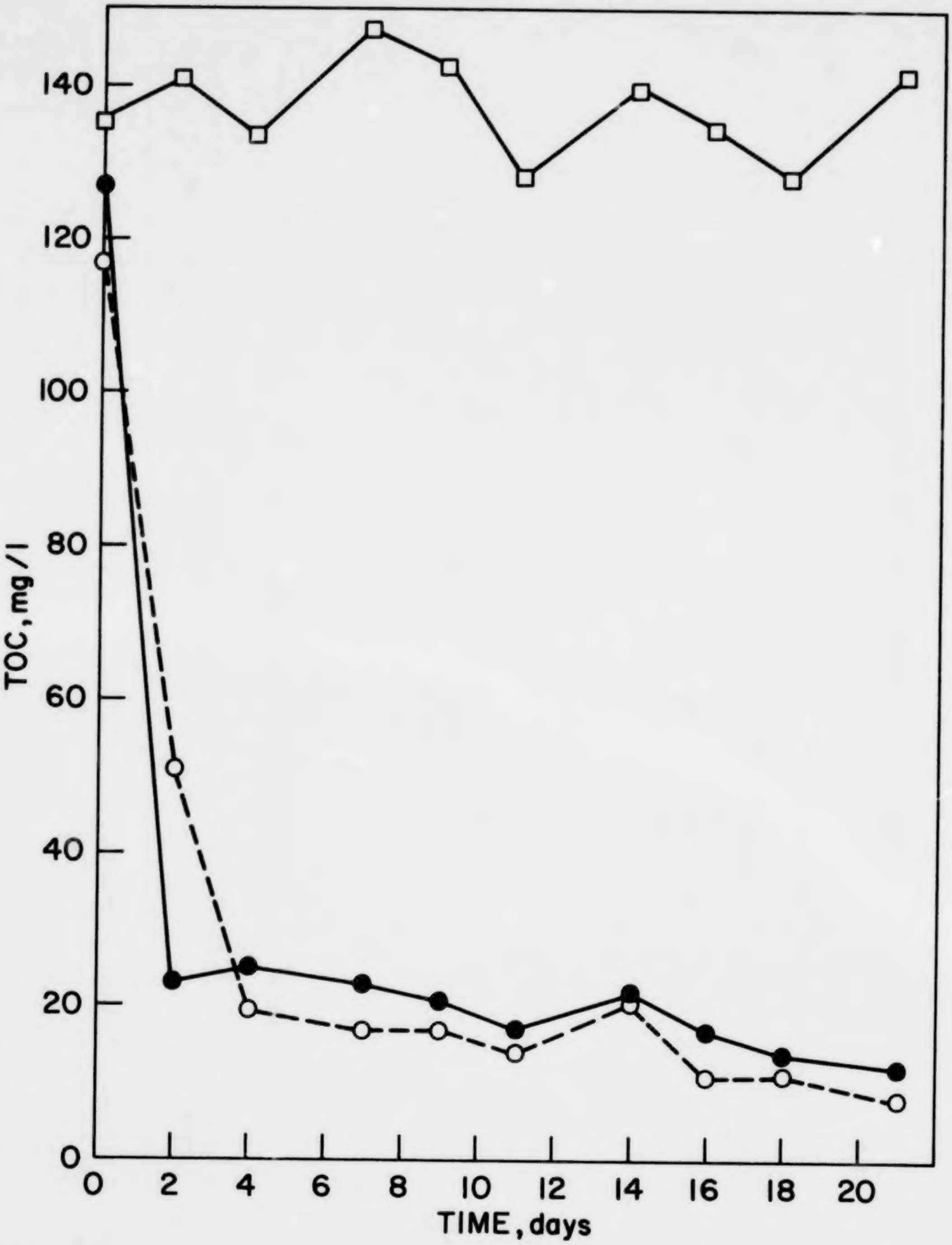

FIGURE 20. Dyeing Wastewater No. 18 (Basic Dyes on Polyester, Atmospheric Exhaust Process): Biodegradation. Unacclimated seed, o; acclimated seed, ●; unseeded, ◻.

TABLE 46. BIOLOGICAL TREATABILITY OF WASTEWATER NO. 19

Set	TOC mg/l Initial	TOC mg/l Final	TOC % Removal	BOD_5 mg/l Initial	BOD_5 mg/l Final	BOD_5 % Removal	Color, ADMI Units Initial	Color, ADMI Units Final	Color, ADMI Units % Removal
A-1	19	0	100	25	1	96	---	---	---
B-1	19	0	100	19	<1	95	---	---	---
C-1	20	12	40	--	--	--	---	---	---
A-10	27	0	100	30	<1	>97	5	Too low for analysis	
B-10	27	1	96	29	<1	>97	12		
C-10	26	22	15	--	--	--	14		
A-100	150	34	77	129	2	98	28	Too low for analysis	
B-100	146	34	77	144	2	99	24		
C-100	155	92	41	---	--	--	27		

TABLE 47. EFFECT OF WASTEWATER NO. 19 ON NITRIFICATION

Set	10% Strength TKN, mg/l Initial	10% Strength TKN, mg/l Final	10% Strength NO_2-N + NO_3-N, mg/l Initial	10% Strength NO_2-N + NO_3-N, mg/l Final	100% Strength TKN, mg/l Initial	100% Strength TKN, mg/l Final	100% Strength NO_2-N + NO_3-N, mg/l Initial	100% Strength NO_2-N + NO_3-N, mg/l Final
A	2.5	2.0	0.3	3.2	10.0	5.0	0.2	0.3
B	2.5	2.0	0.1	3.6	9.5	7.5	0.2	1.1
C	2.5	2.0	<0.1	<0.3	7.5	6.8	<0.1	<0.3

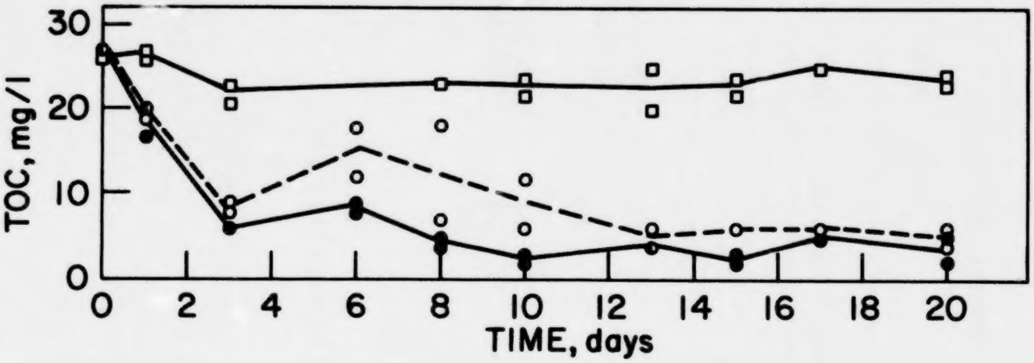

FIGURE 21. Dyeing Wastewater No. 19 (Disperse, Acid, and Basic Dyes on Polyamide Carpet, Kuster Process): Biodegradation. Unacclimated seed, o; acclimated seed, ●; unseeded, □.

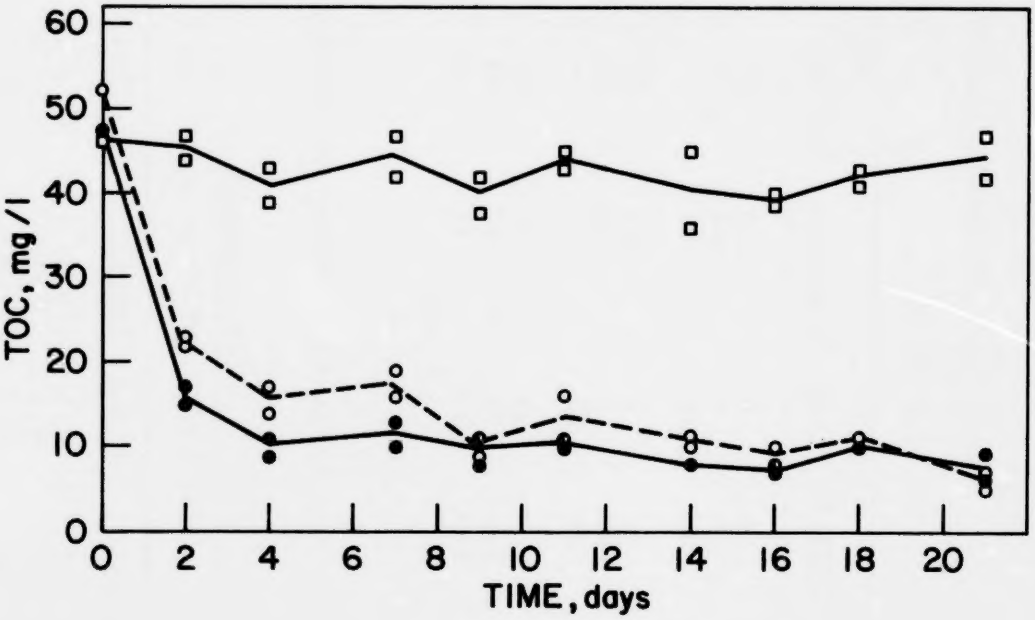

FIGURE 22. Dyeing Wastewater No. 20 (Naphthol on Cotton, Exhaust Procedure): Biodegradation. Unacclimated seed, o; acclimated seed, ●; unseeded, □.

TABLE 48. BIOLOGICAL TREATABILITY OF WASTEWATER NO. 20

	TOC			BOD_5			Color, ADMI Units		
	mg/l			mg/l					
Set	Initial	Final	% Removal	Initial	Final	% Removal	Initial	Final	% Removal
A-1	47	0	100	61	<1	>98	---	---	---
B-1	43	2	95	34	<1	>97	---	---	---
C-1	36	30	17	--	--	--	---	---	---
A-10	52	6	88	59	<1	>98	340	212	38
B-10	47	8	83	44	<1	>98	297	229	23
C-10	46	44	4	--	--	--	349	280	20
A-100	174	58	67	204	3	99	2,850	509	82
B-100	176	55	69	216	<1	100	2,805	497	82
C-100	173	158	9	---	--	---	2,619	537	80

TABLE 49. EFFECT OF WASTEWATER NO. 20 ON NITRIFICATION

	10% Strength				100% Strength			
	TKN, mg/l		NO_2-N + NO_3-N, mg/l		TKN, mg/l		NO_2-N + NO_3-N, mg/l	
Set	Initial	Final	Initial	Final	Initial	Final	Initial	Final
A	7.0	5.0	1.6	8.0	24.5	21.8	13.0	13.5
B	7.5	5.8	1.7	6.9	31.5	27.5	13.0	12.8
C	6.0	7.3	1.5	1.5	25.0	25.0	13.0	12.8

than at 10% and occurred in both seeded and unseeded flasks. It is thought that the lower solubility of the color at full-strength may be responsible for the unusual results obtained. The red color was easily removed on standing or by filtration, yielding a clear straw-colored solution. Insufficient data were available to determine the effect of this wastewater on nitrification (Table 49).

CONCLUSIONS

Overall, the following conclusions were reached:

(1) in most cases biological treatment of dyeing wastewaters, while inadequate for color removal, can achieve high (≥90%) levels of soluble BOD removal

(2) in one case, the dyeing wastewater was inhibitory to removal of BOD, even at low strengths, possibly indicating the need for segregating this wastewater from biological treatment systems

(3) biological treatment alone appears to be inadequate for color removal

(4) in at least 10 cases, the dyeing wastewaters are inhibitory to nitrification, or at least have organic nitrogen components not susceptible to nitrification, a factor which must be considered if effluent standards require low levels of Kjeldahl nitrogen

(5) there was little or no consistency among dyeing classes in relation to effect on BOD, TOC, color, or ammonia removal.

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SECTION VII

PHYSICAL-CHEMICAL TREATMENT: COAGULATION, ADSORPTION, OZONATION

In order to determine if the twenty dyeing wastewaters could be treated by coagulation, adsorption, and chemical oxidation, a series of laboratory-scale treatability studies was conducted. The primary objectives of the treatment were decolorization of the wastes and removal of total organic carbon (TOC). Lime, aluminum salts, and ferric iron salts were investigated as coagulants. Different types of powdered activated carbon (PAC) were investigated as adsorbents. Ozone was investigated as a chemical oxidant. It should be emphasized that the treatability analysis was carried out on a laboratory scale only, on dyeing wastewaters generated from the dyeing operation only, and that the objective of the study was to determine if the wastes were treatable and, if so, by what method and under what conditions. The results should not be used directly to design a facility for the treatment of segregated dyeing wastewaters at the chemical doses given, but should serve only as a guide in selecting the most appropriate treatment method and chemical conditions; the actual chemical requirements must still be determined by appropriate test procedures.

This section of the report details the procedures and results of the physical-chemical treatability studies.

PROCEDURES

Following receipt and storage of the wastes as described in Section V, the samples were brought to room temperature. The coagulation and powdered carbon adsorption studies were performed using conventional jar test procedures. The ozonation studies were performed in a small diffused aeration column using ozone from a laboratory ozone generator.

Coagulation

In the case of lime (CaO), various amounts were weighed out and each dose added to a 500 ml sample of the dyeing wastewater. A magnetic stirrer was used to flash mix each sample until the pH stabilized, after which the sample was stirred slowly for 30 minutes, at 35 rpm, on the jar test apparatus. Each sample was allowed to settle for 30 minutes and aliquots of the supernatant were withdrawn for subsequent ADMI color and TOC analyses by the procedures described in Section V.

When aluminum and ferric iron were used, various amounts of the coagulants were added from stock solutions of alum ($Al_2(SO_4)_3 \cdot 18\ H_2O$) and ferric chloride ($FeCl_3$) to 500 ml samples of the dyeing wastewaters, and each sample was flash mixed to provide complete dispersal of the coagulant. The pH of each sample was kept at the desired value by concurrent addition of either Na_2CO_3 or H_2SO_4 during flash mixing. Experiments were conducted at several pH values in the pH 5 to 7 range. After flash mixing, each sample was stirred for 30 minutes at 35 rpm and allowed to stand quiescently for 30 minutes. After the floc settled, aliquots were withdrawn for ADMI color and TOC analyses. It should be mentioned that the method of adding alum or iron to disperse dyeing wastewaters was found to be very critical in effecting satisfactory treatment by coagulation. Good flash mixing was required in order to insure uniform dispersal of the coagulant. It was observed that in disperse dye systems which were not properly rapid-mixed, the concentrated coagulant solution which was added tended to form a separate layer on top of the wastewater and the suspension remained turbid.

Adsorption

Various amounts of powdered activated carbon (PAC) were weighed out and added to 500 ml samples of the dyeing wastewater. The carbon was dispersed using a magnetic stirrer and each sample was stirred for 60 min. at 35 rpm on the jar test apparatus to keep the PAC suspended and to provide sufficient contact of the suspended carbon with the wastewater. After mixing, the carbon was separated from the wastewater by filtering the samples through Reeve Angel glass fiber filters, and the filtrate was analyzed for ADMI color and TOC. Experiments were repeated using different types of powdered activated carbon, and the effect of pH on adsorption was studied by pre-adjustment of the sample pH with Na_2CO_3 or H_2SO_4 during the rapid mix. The characteristics of the powdered carbons investigated are given in Appendix D.

Ozonation

Six liters of the dyeing wastewater was placed in an aeration column and treated with ozone generated by passing oxygen through a W. R. Grace and Co. ozone generator (Model LG-2-L1). The aeration column was 4 in. in diameter and 5 ft high, fitted with a stainless steel fine mesh disc gas diffuser. A sampling port was located 6 in. from the bottom of the column and the liquid level of the 6 liter sample was approximately 3 ft. After setting the rotometer to establish the desired gas flow rate (usually 5-10 standard cu ft/hr) using oxygen only, the ozone generator was turned on. Samples were taken from the column at various time intervals for subsequent analysis of ADMI color, TOC, and pH. At the conclusion of the ozonation period, the gas flow to the column was turned off and passed via a 3-way valve through a solution of 0.1N neutral buffered potassium iodide solution for a specified time period (usually 2 min.) to measure the ozone content of the gas stream. (The pressure drop through the KI had previously been balanced against the pressure drop through the column to insure the same gas flow rate through each system.) The iodine formed was subsequently titrated with standardized sodium thiosulfate. An example calculation for determining the ozone content of the gas stream is given in Appendix E. The experimental set-up is shown in Figure 23; all tubing and connections were stainless steel or Teflon.

Ozonation studies were conducted on some of the wastes at different gas flow rates and at different partial pressures of ozone in the gas stream. The effect of pH was also investigated by adjusting the pH of the 6 liter sample with H_2SO_4 or NaOH prior to ozonation. No attempt was made to optimize gas transfer by modifying the diffuser or the reactor configuration.

RESULTS

This section describes the results of the physical-chemical treatability studies. The results of treating each dyeing wastewater are reported here and overall considerations regarding physical-chemical treatment are discussed in Section VIII. All doses of alum are reported in mg/l as Al; ferric iron is reported in mg/l as Fe; lime doses are reported in mg/l as CaO.

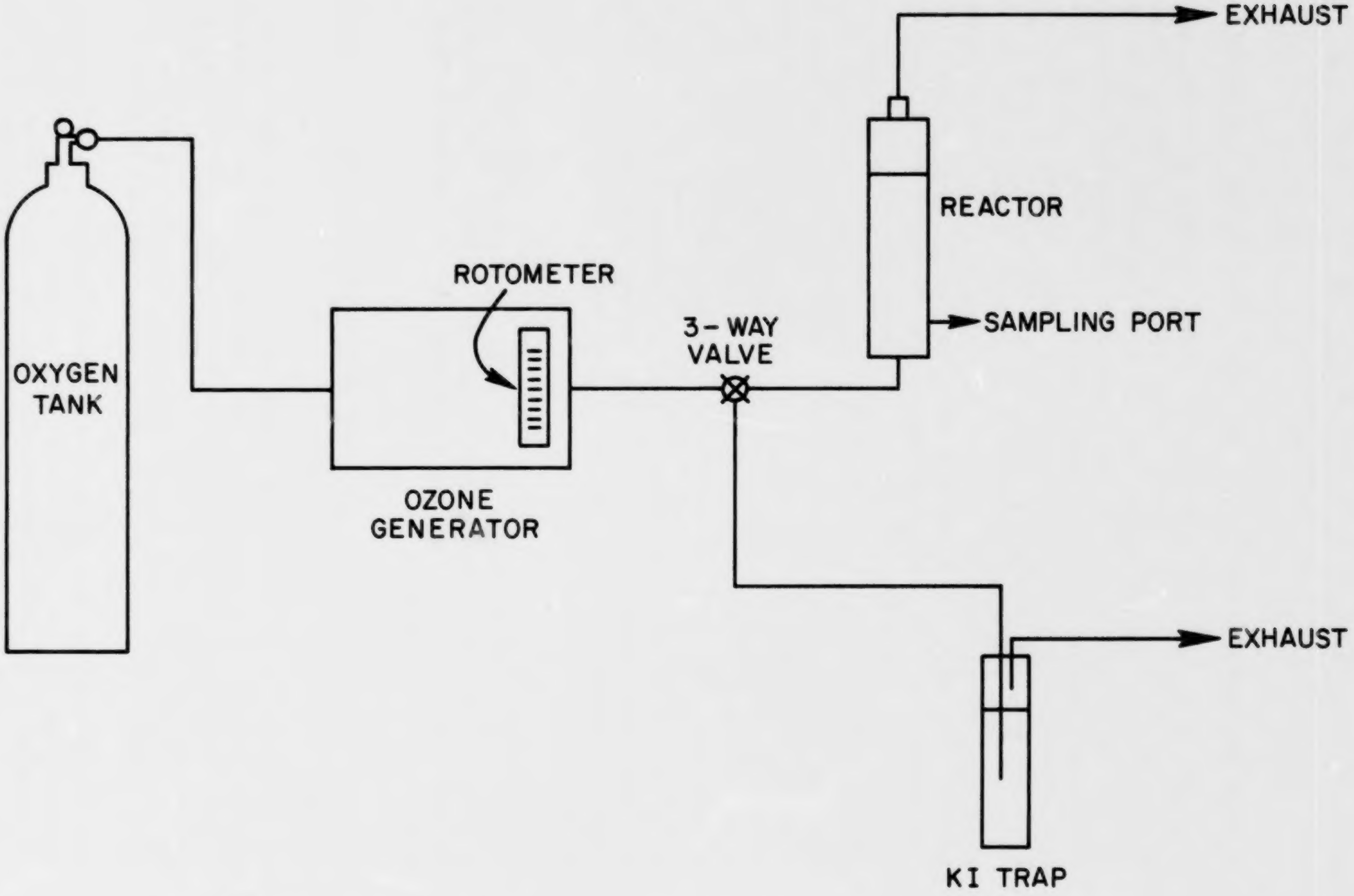
EXHAUST
REACTOR
SAMPLING PORT
OXYGEN TANK
ROTOMETER
3- WAY VALVE
OZONE GENERATOR
EXHAUST
KI TRAP

FIGURE 23. Schematic Diagram of Apparatus for Ozonation Study

Dyeing Wastewater No. 1. Vat Dyes on Cotton - Exhaust

Figure 24 shows the results of treating the vat dyeing wastewater by coagulation using lime and alum. (The initial color of the waste sample prior to treatment by coagulation (1,000 ADMI color units) was somewhat different than the raw color value of the fresh waste (1910 ADMI color units) reported in Section V, reflecting some degree of instability of the waste during storage.) Alum effectively decolored the waste at a pH of 6.3 (alum coagulation is generally most effective in the pH range 5.0 to 7.0); approximately 140 mg/l of alum (as Al) was required to decolorize the waste to 100 color units. Lime was not as effective; 1,000 mg/l as CaO (pH 12.0) reduced the color to only about 350. (It should be recalled that all measurements of color were made at pH 7.6 in accordance with the standard ADMI color procedure despite treatment at another pH value.) The reduction in total organic carbon as a result of coagulation by alum and lime is shown in Figure 25; since both studies were performed on the same day, no explanation for the difference in starting TOC concentrations is available except that vat dyes tend to separate from solution to some extent and a representative sample may not have been obtained. The concentration of TOC was reduced about 30% and 50% by 1,000 mg/l of lime and 160 mg/l of Al, respectively.

Powdered activated carbon (Darco HD-3000) was relatively ineffective, with doses up to 4 g/l at a pH of 11.1 providing no visual color change in the waste. No additional carbon adsorption studies at lower pH values were done for this wastewater.

Dyeing Wastewater No. 2. 1:2 Metal Complex Dye on Polyamide - Exhaust

Coagulation with alum provided very little color reduction. Applications of aluminum up to 160 mg/l at pH 6.3 reduced the color approximately 30% to about 230. Essentially no reduction in TOC was measured. Similarly lime, at doses up to 1,000 mg/l (pH 11.2), reduced the final color to only about 230 (see Figure 26); there was no change in TOC.

Figure 26 shows the effect of powdered activated carbon adsorption on the acid black dye waste. Nine hundred mg/l of Nuchar D-16 decolorized the sample to a final color value of less than 100 at pH 6.8 (the pH of the raw waste). TOC reduction was small, as shown in Figure 27, with only

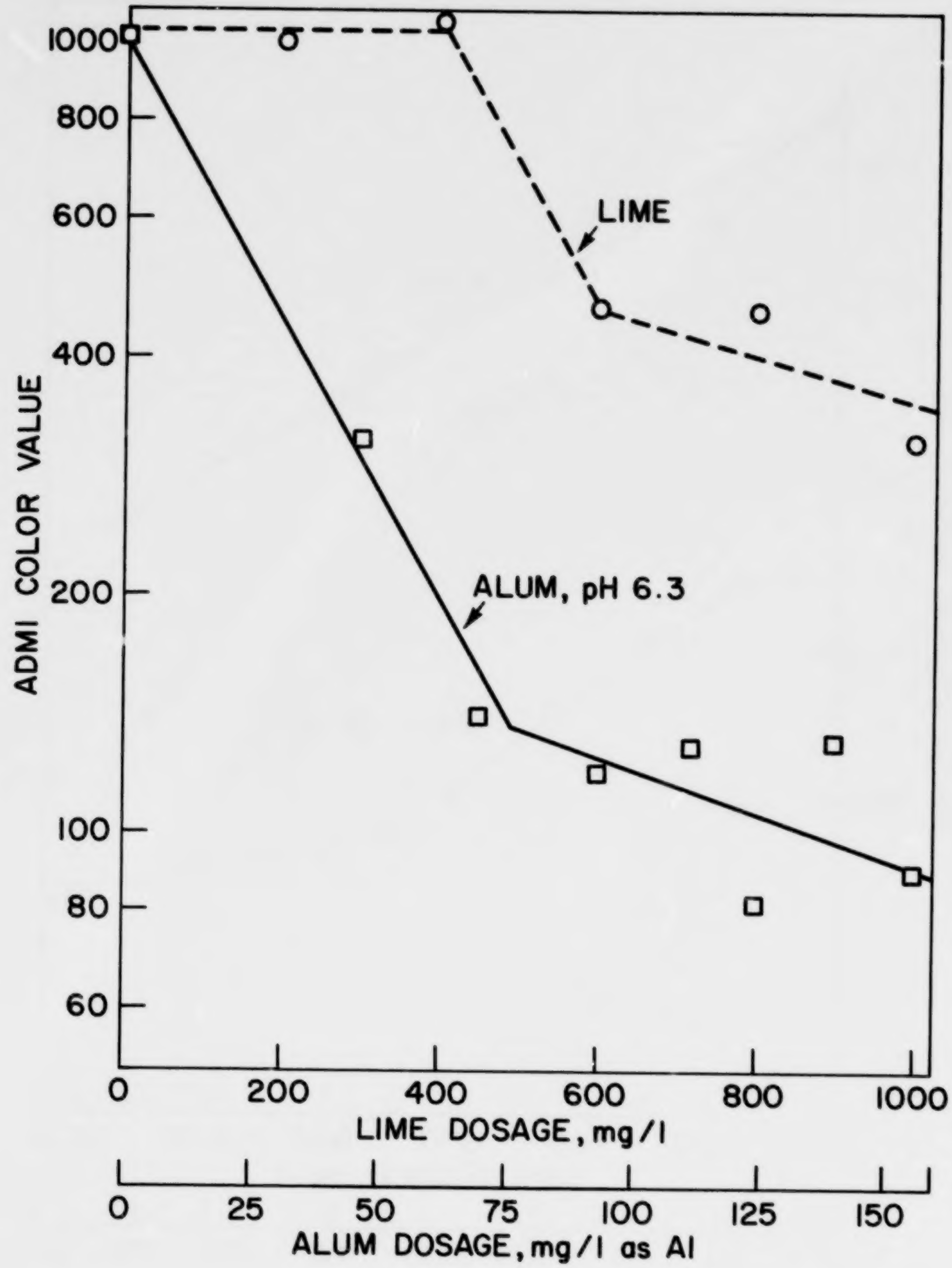

FIGURE 24. Dyeing Wastewater No. 1 (Vat Dyes on Cotton): Decolorization by Lime and Alum Coagulation

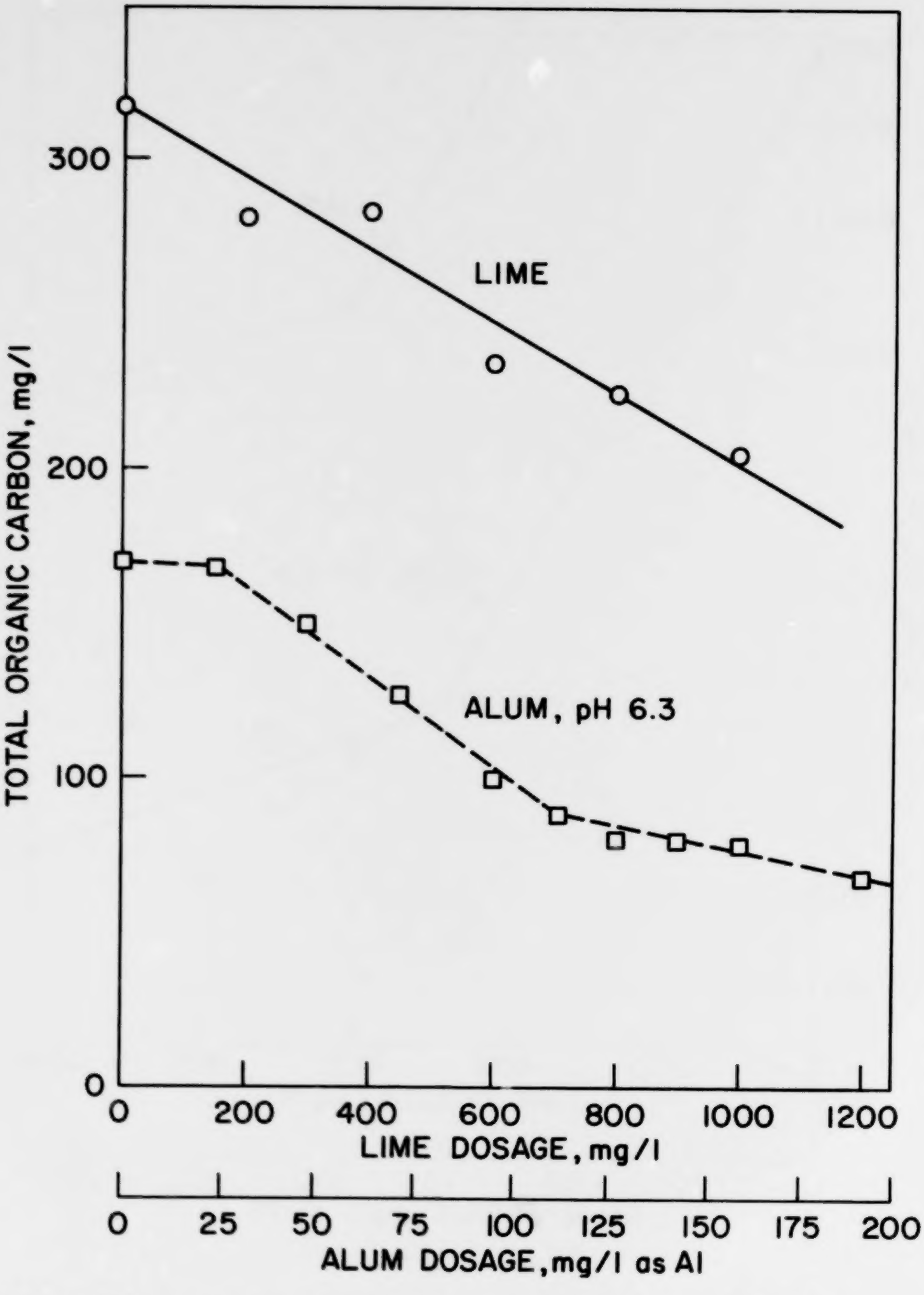

FIGURE 25. Dyeing Wastewater No. 1 (Vat Dyes on Cotton): Total Organic Carbon Reduction by Lime and Alum Coagulation

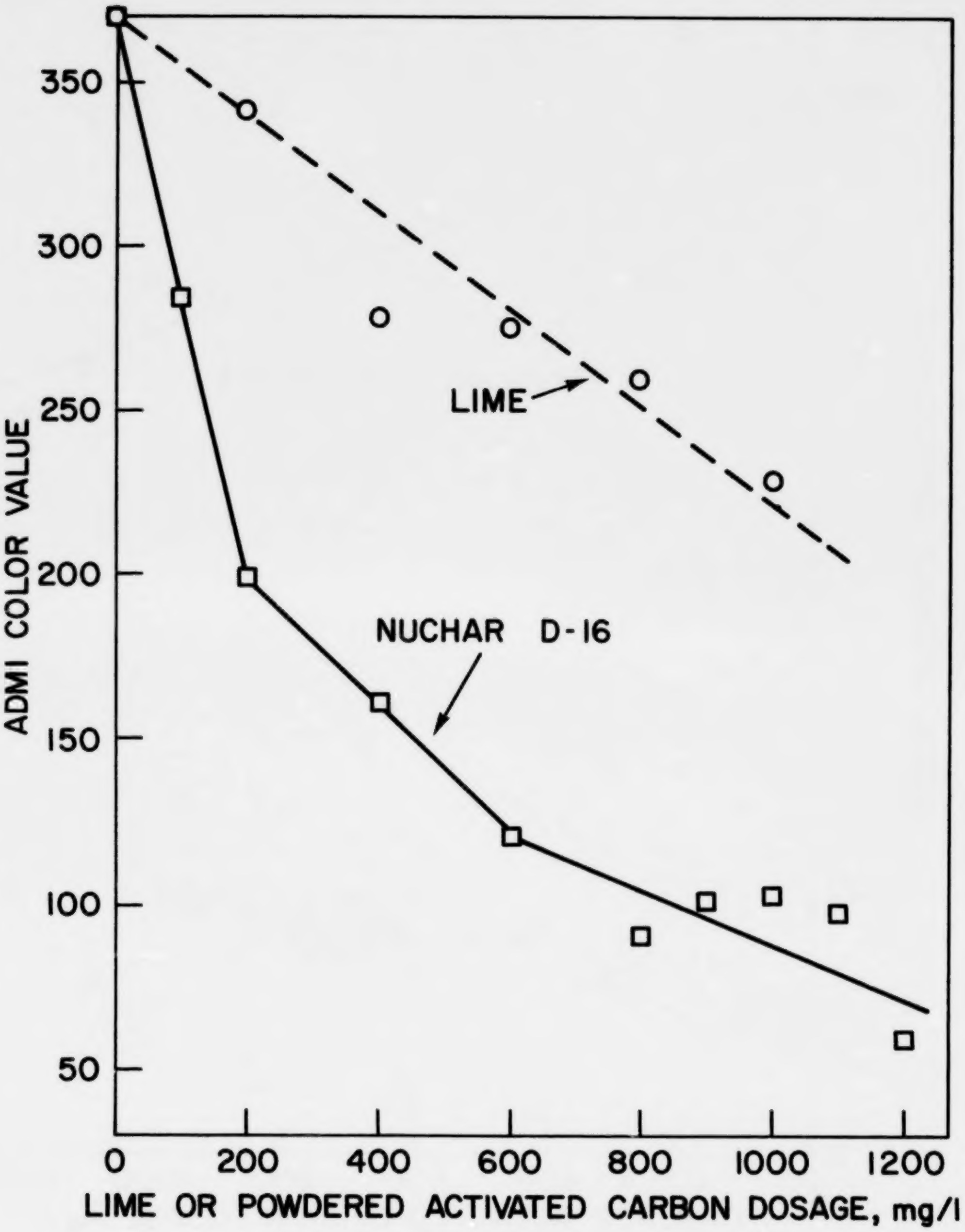

FIGURE 26. Dyeing Wastewater No. 2 (1:2 Metal Complex Dye on Polyamide): Decolorization by Lime and Powdered Activated Carbon Adsorption

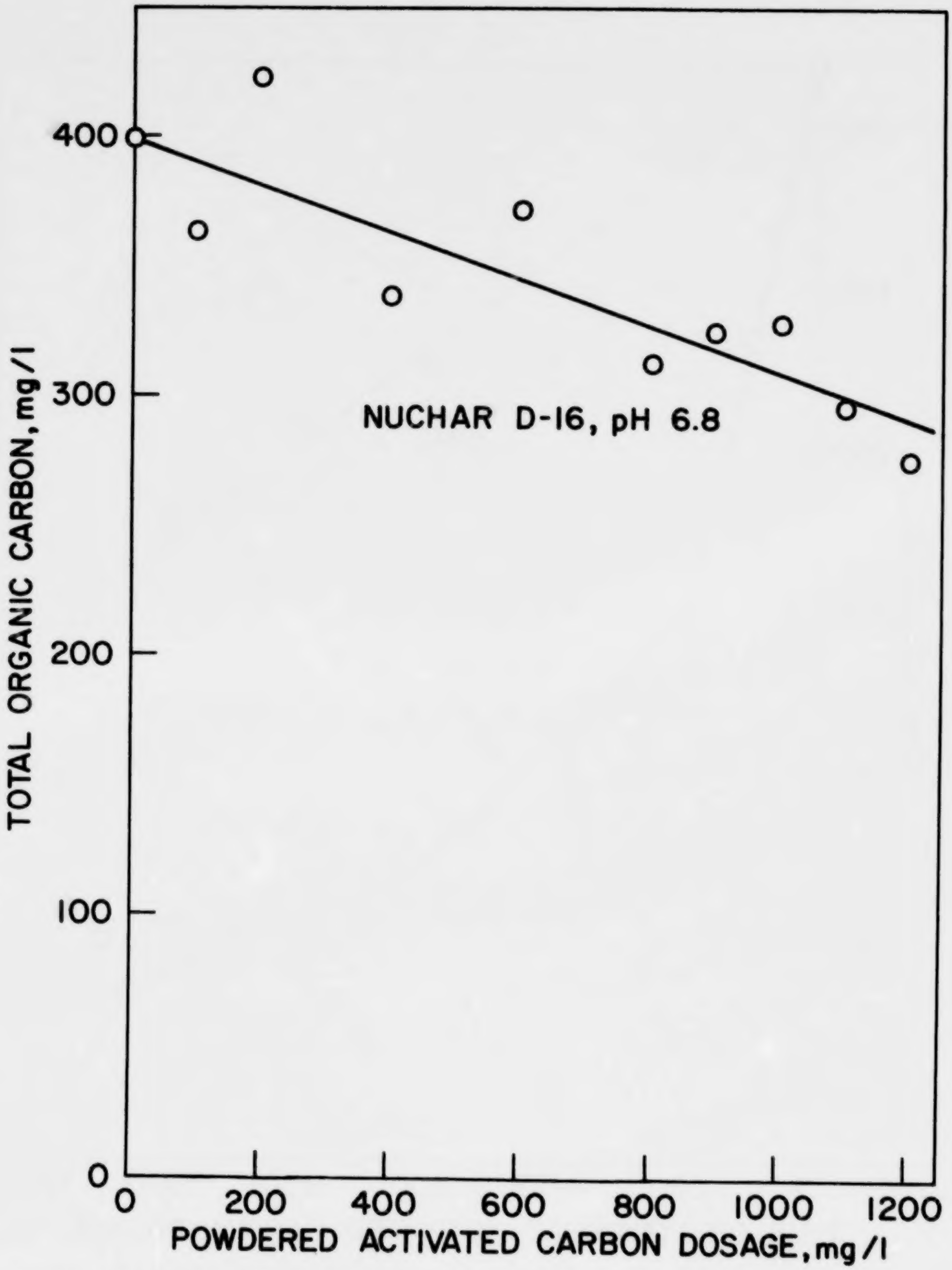

FIGURE 27. Dyeing Wastewater No. 2 (1:2 Metal Complex on Polyamide): Removal of Total Organic Carbon by Powdered Activated Carbon

a 20% reduction in TOC resulting from the application of 1,000 mg/l of Nuchar D-16, suggesting that the dye is significantly more strongly adsorbed than the other organic components of the dye bath.

Ozone was found to effectively decolorize the waste as shown in Figure 28. The application of only 800 mg of ozone (approximately 130 mg/l) was sufficient to decolorize the sample to less than 100. The pH dropped slightly from 7.9 to 7.6 during the 20 minute treatment, but TOC remained virtually unchanged. (The low ozone yield of 1.8% O_3 by volume was due to a leak in the generator which was subsequently repaired.)

Dyeing Wastewater No. 3. Disperse Dyes on Polyester - Exhaust

Figure 29 shows the effect of coagulation in decolorizing the disperse dyeing wastewater. Alum was very effective, with doses of approximately 60 mg/l of Al reducing the color to less than 50 at a pH of 5. Coagulation studies were also conducted at pH 6 and pH 7 with the results at pH 6 being very similar to those shown for pH 7 (see also Table 50); it is apparent that alum performs more effectively at pH 5. Tests at pH values below 5 showed little apparent reduction in color. Ferric iron was also relatively effective in decoloring the disperse dyeing wastewater; 260 mg/l of Fe(III) was sufficient to reduce the color of the waste to less than 50 at a pH of 5. In the case of iron, however, when the system was underdosed, an enhancement in color was measured due to the presence of reddish-brown colloidal particles of ferric hydroxide. Iron was also less efficient at higher pH's as shown by Table 50. Lime gave no apparent change in color at dosages up to 1,000 mg/l (pH 11.9). TOC was reduced approximately 50-60% at Al and Fe(III) dosages of 160 and 340 mg/l, respectively (see Table 50); TOC removal with iron was slightly better than with aluminum. No TOC reduction was observed when lime was used.

Application of powdered activated carbon (Nuchar D-16 at pH 7.8, the pH of the raw dye waste) gave no apparent decolorization at doses up to 1200 mg/l.

Figure 30 shows the results of ozonating the disperse dyeing wastewater. Relatively poor decolorization was observed; even after the application of 37 gm of ozone (approximately 6 gm/l), the color was reduced by only

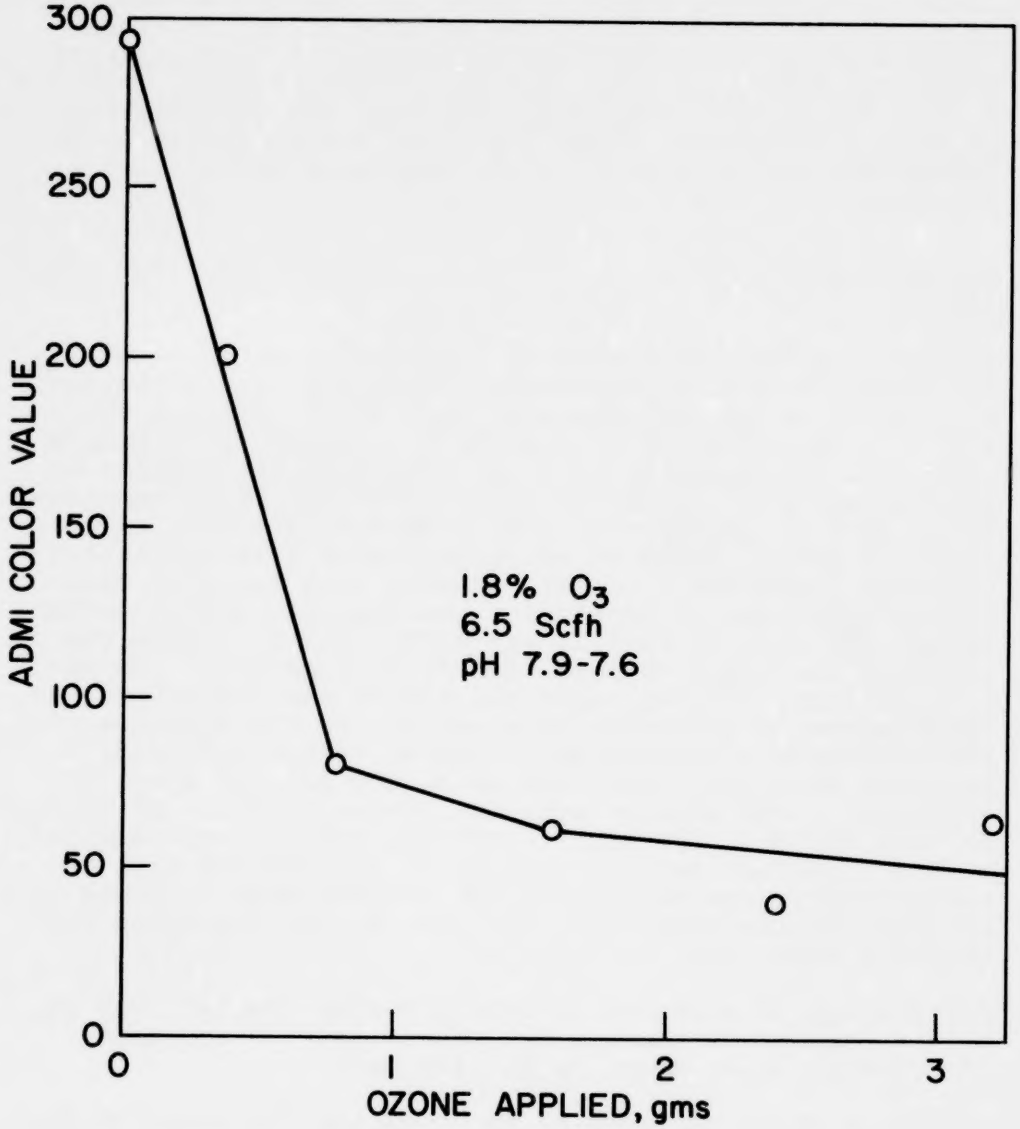

FIGURE 28. Dyeing Wastewater No. 2 (1:2 Metal Complex Dye on Polyamide): Decolorization by Ozone

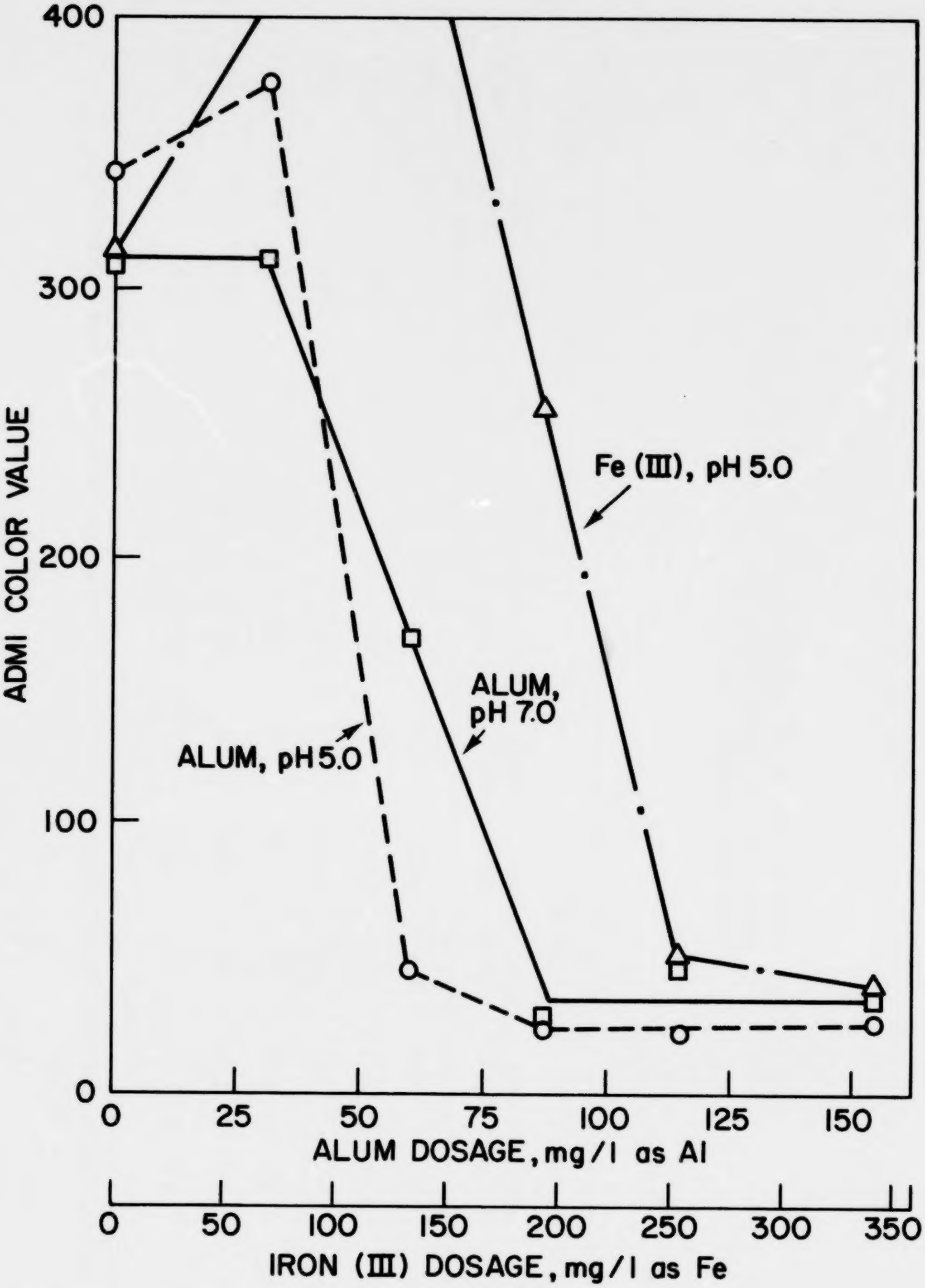

FIGURE 29. Dyeing Wastewater No. 3 (Disperse Dyes on Polyester): Decolorization by Alum and Iron (III) Coagulation

TABLE 50. EFFECT OF pH ON COAGULATION OF DYEING WASTEWATER NO. 3 (DISPERSE DYES ON POLYESTER) BY ALUM AND FERRIC CHLORIDE

Alum dose, mg/l as Al	pH 7[a]		pH 6[a]		pH 5[a]		Fe(III) dose, mg/l as Fe	pH 6[a]		pH 5[a]	
	ADMI color	TOC, mg/l	ADMI color	TOC, mg/l	ADMI color	TOC, mg/l		ADMI color	TOC, mg/l	ADMI color	TOC, mg/l
0	306	308	324	321	345	305	0	387	300	313	294
31	310	274	350	315	375	297	67	---	296	---	302
61	172	215	149	185	43	173	132	---	280	---	281
90	27	176	19	175	26	159	195	545	188	261	153
117	43	152	36	160	20	167	255	70	148	47	127
157	34	134	23	150	28	159	341	27	133	37	114

[a] pH maintained constant by concurrent addition of acid or base with the coagulant.

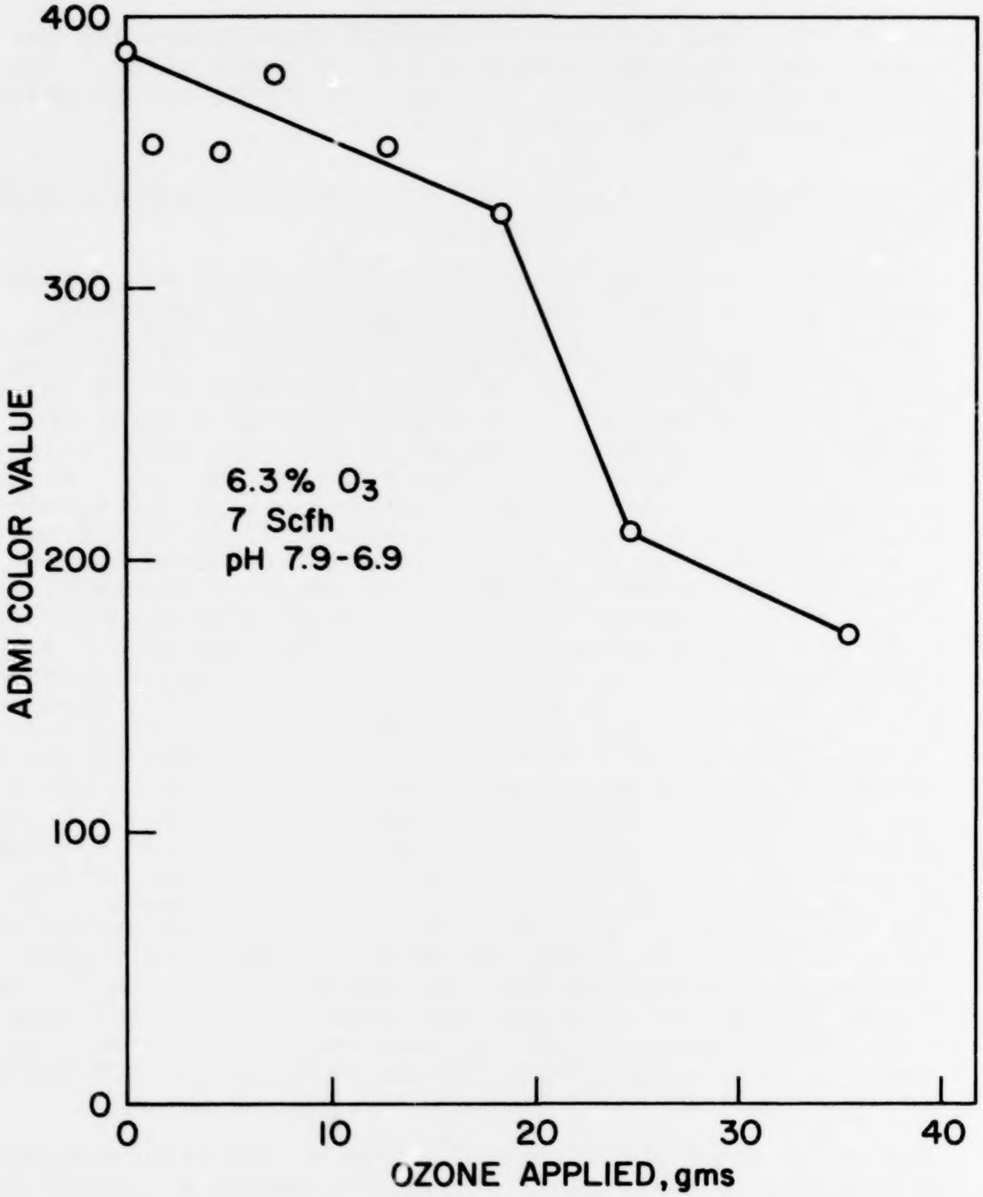

FIGURE 30. Dyeing Wastewater No. 3 (Disperse Dyes on Polyester): Decolorization by Ozone

about 55%. The Figure also shows a significant lag period before any appreciable decolorization takes place. The pH dropped somewhat during treatment and there was no measurable change in TOC.

Dyeing Wastewater No. 4. After-Copperable Direct Dye on Cotton - Exhaust

The after-treatable direct dyeing wastewater was a relatively turbid sample (the concentration of suspended solids was 41 mg/l), with most of the color associated with the suspended particles in the waste. As reported in Section V, prefiltration of the sample with Celite removed most of the color and, as a result, the data reported herein are for samples analyzed by the ADMI color procedure in which the prefiltration step was omitted. Although some of the colored particles settled out of the sample upon standing, an appreciable quantity of colloidal particles with their associated color still remained and it appeared that coagulation would be the best treatment alternative. Figure 31 shows the results of coagulating the waste with alum and with lime. The ordinate, i.e., "apparent" color, is an indication of the visual appearance of the sample, but it must be recalled that this apparent color value includes light scattering due to suspended particulates as well as the absorbance of light by the dye molecules and copper salts. Lime, at doses up to 200 mg/l (pH 11.1), resulted in decolorization of the waste to an apparent color of about 120. The resulting floc settled more slowly than the floc formed by alum. Coagulation with alum resulted in decolorization of the waste to an apparent color of less than 100 at an aluminum dosage of 16 mg/l at pH 6.0. Coagulation with alum at pH 6 gave appreciably better results than coagulation at pH 7. Increasing doses of alum also resulted in better-settling floc. The removal of TOC by alum and lime was small as shown in Figure 32. There was no reduction in BOD following the application of 16 mg/l of aluminum at pH 6.

Figure 33 shows the effect of ozone on the after-copperable direct dyeing wastewater. Ozone was fairly efficient in decolorizing the blue waste, with 2.5 gms of ozone (approximately 400 mg/l) reducing the apparent color to less than 100. pH remained constant throughout the ozonation period. There was no measurable change in TOC.

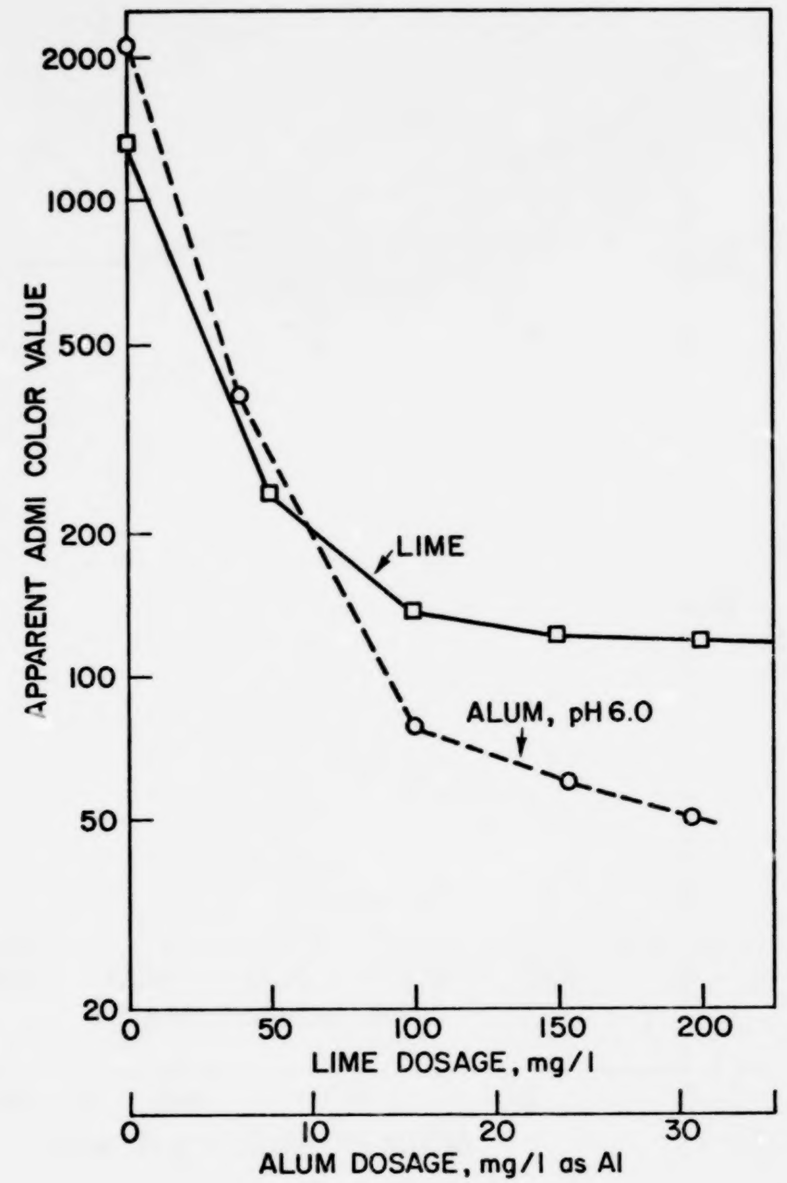

FIGURE 31. Dyeing Wastewater No. 4 (After-Copperable Direct Dye on Cotton): Color Removal by Lime and Alum Coagulation

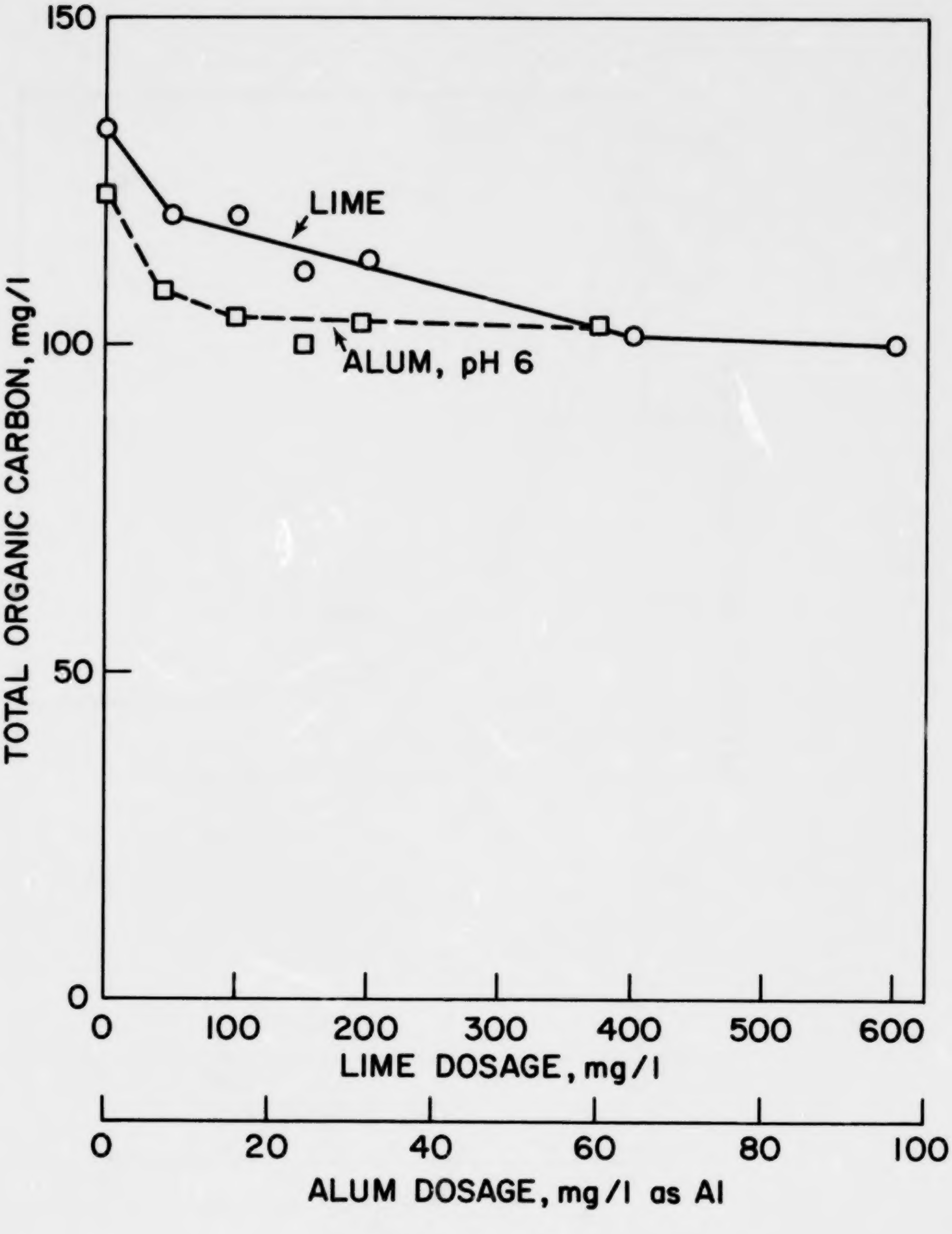

FIGURE 32. Dyeing Wastewater No. 4 (After-Copperable Direct Dye on Cotton): Removal of Total Organic Carbon by Lime and Alum Coagulation

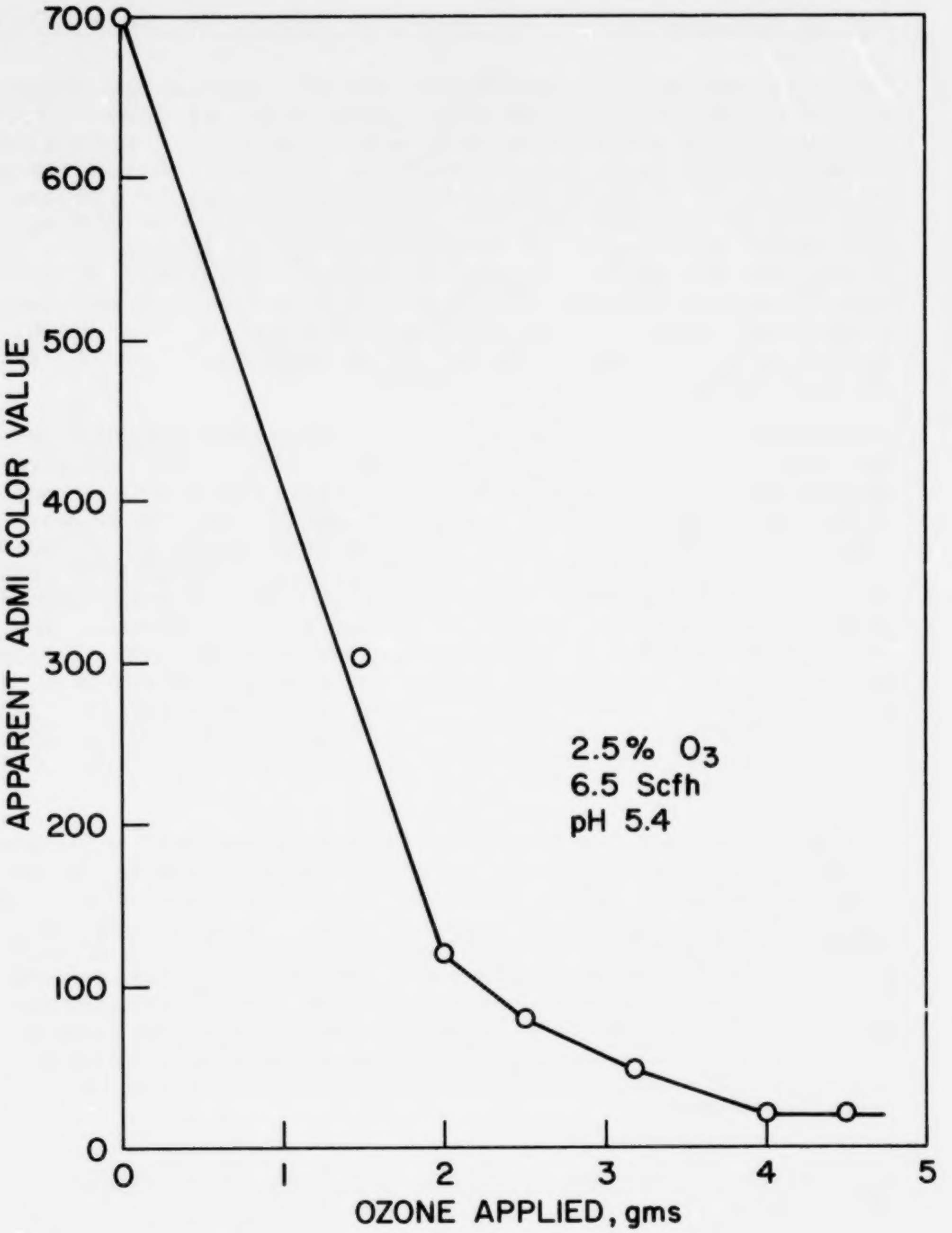

FIGURE 33. Dyeing Wastewater No. 4 (After-Copperable Direct Dye on Cotton): Decolorization by Ozone

Dyeing Wastewater No. 5. Reactive Dye on Cotton - Exhaust

The reactive dyeing wastewater had an intense red color, as reflected by its high ADMI color value of 3890. Coagulation of the waste with alum was relatively ineffective as shown in Figure 34; 160 mg/l of Al(III) reduced the ADMI color to 635 at pH 5 but the color could not be reduced any further by additional Al(III) dosages up to 450 mg/l. Treatment by alum at pH 7 gave no decolorization at a dosage of 160 mg/l. Figure 34 shows a reduction of TOC by alum of approximately 30-50% at pH 5 depending upon the alum dose; there was no change in TOC at pH 7 as shown. Application of lime at doses up to 3000 mg/l (pH 11.8) gave no measurable reduction in color.

Activated carbon was particularly effective in decoloring the reactive dye, but large doses of the carbon were required as indicated in Figure 35. The adsorption studies were conducted at three different pH values, as shown, using Darco HD-3000. Best results were obtained at pH 3.5 (the raw dye waste had a pH of 11.2); approximately 2000 mg/l reduced the ADMI color value to 100. Higher carbon doses were required at pH 10.7 and pH 7 as shown. The removal of TOC by carbon was also quite effective as shown in Figure 36, again with increased removal obtained at the more acidic pH value; 2000 mg/l of HD-3000 at pH 3.5 reduced the TOC concentration by 80% to 28 mg/l. The discrepancy in the initial TOC concentrations in Figure 36 could not be explained.

The reactive red dye was decolorized quite well by ozone as shown in Figure 37; an application of 6 gms of ozone (approximately 1 gm/l) resulted in decolorization to less than 100 color units at a pH of 10.6. Despite the lower percentage of ozone in the gas stream at pH 10.6 than at pH 2.0, decolorization was more effective at the higher pH value. (The ozone generator still leaked considerably as evidenced by the low ozone yields.) A third sample, at pH 8, was also decolorized less effectively than at pH 10.7. The concentration of TOC was unchanged by the ozone treatment.

Dyeing Wastewater No. 6. Disperse Dyes on Polyamide Carpet - Exhaust

Figure 38 shows the effect of lime and alum in coagulating the disperse dyeing wastewater; the waste was relatively uncolored, having an ADMI color value of 100. Following

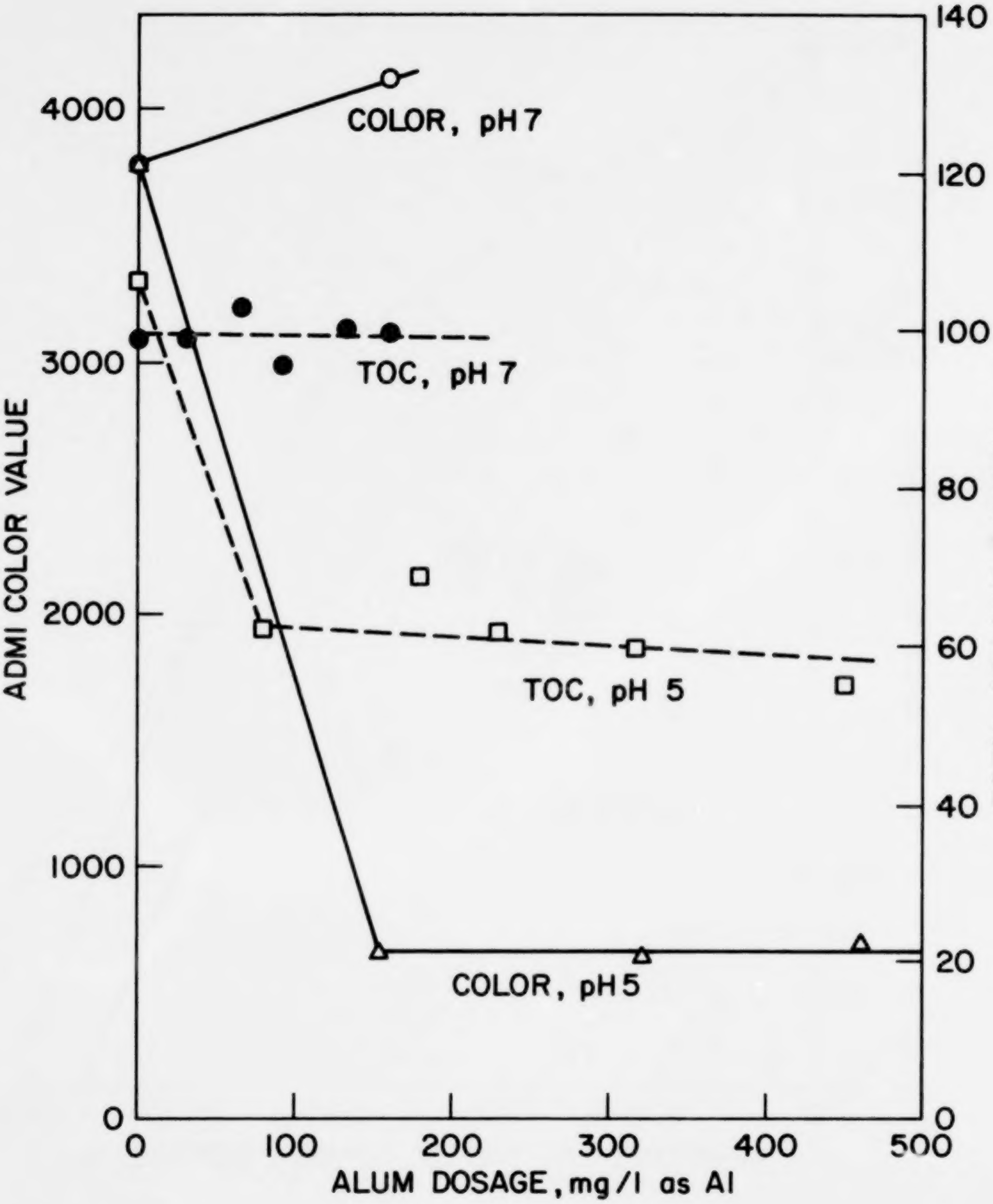

FIGURE 34. Dyeing Wastewater No. 5 (Reactive Dye on Cotton): Color and Total Organic Carbon Removal by Alum

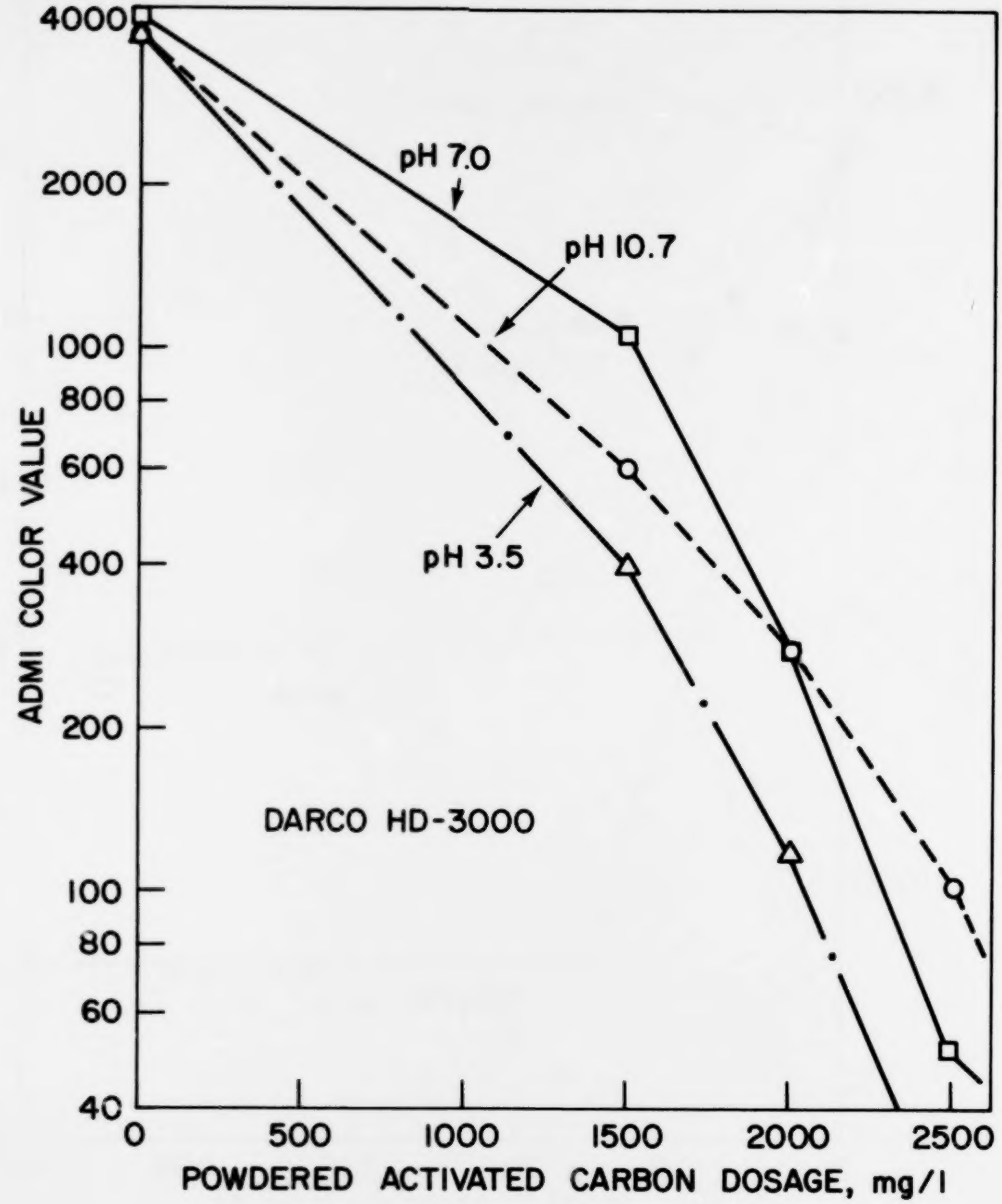

FIGURE 35. Dyeing Wastewater No. 5 (Reactive Dye on Cotton): Decolorization by Powdered activated Carbon Adsorption

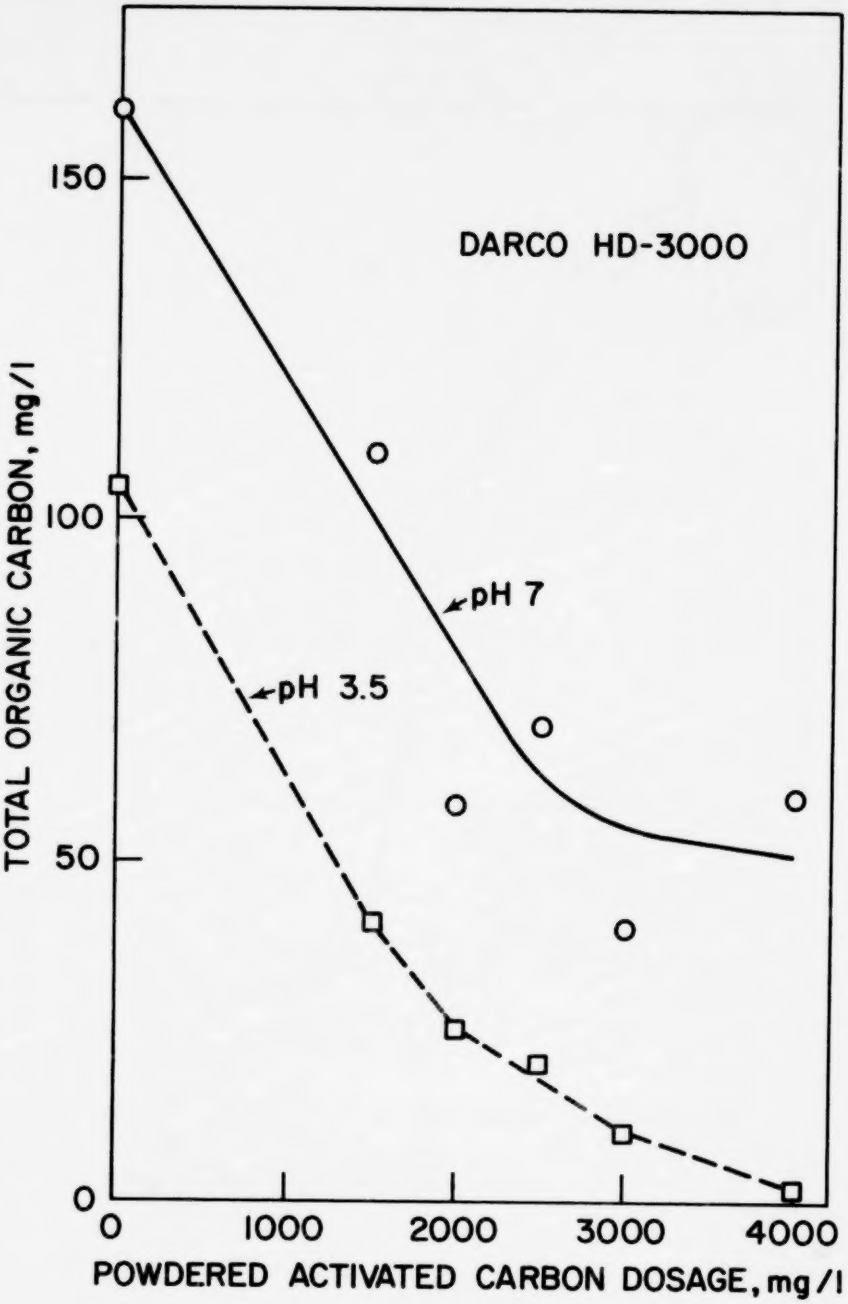

FIGURE 36. Dyeing Wastewater No. 5 (Reactive Dye on Cotton): Total Organic Carbon Removal by Powdered Activated Carbon

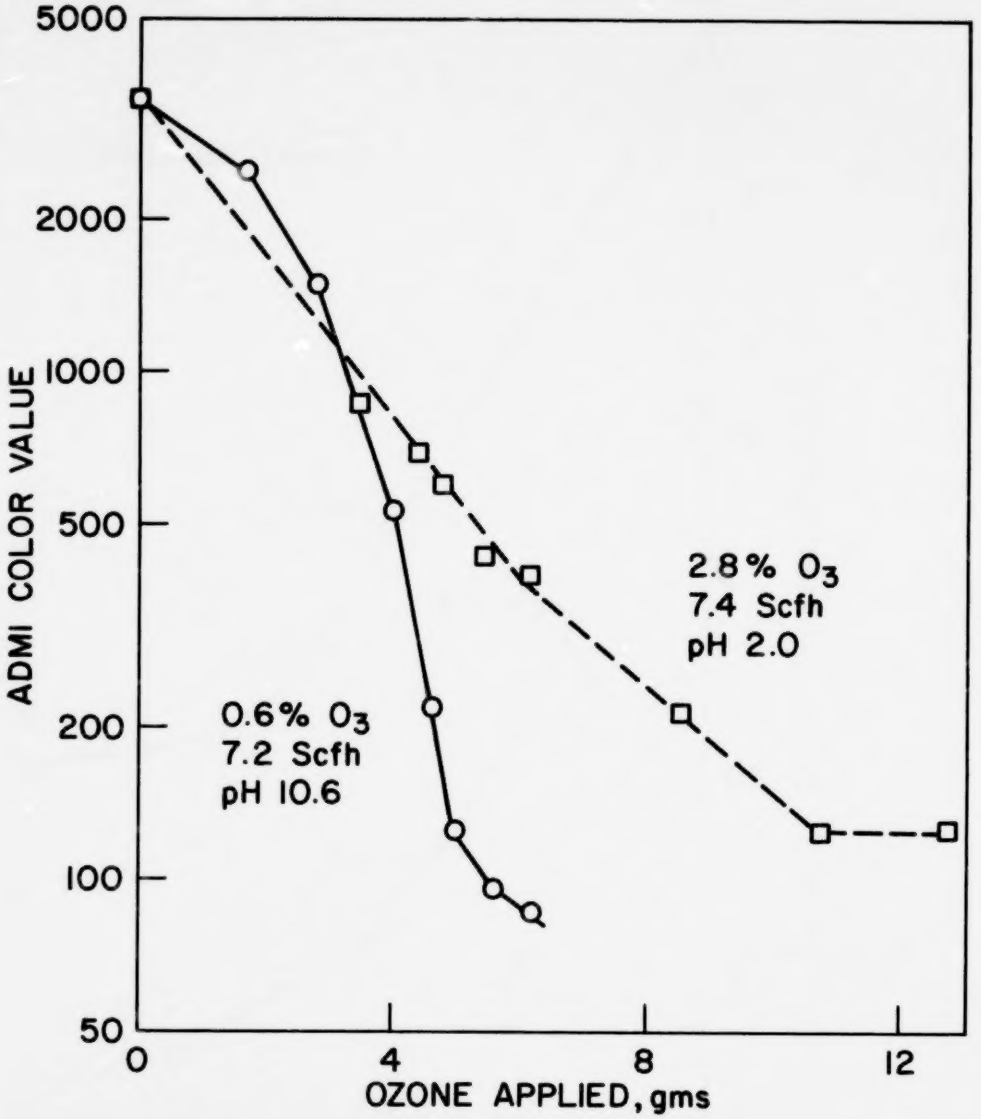

FIGURE 37. Dyeing Wastewater No. 5 (Reactive Dye on Cotton): Decolorization by Ozone

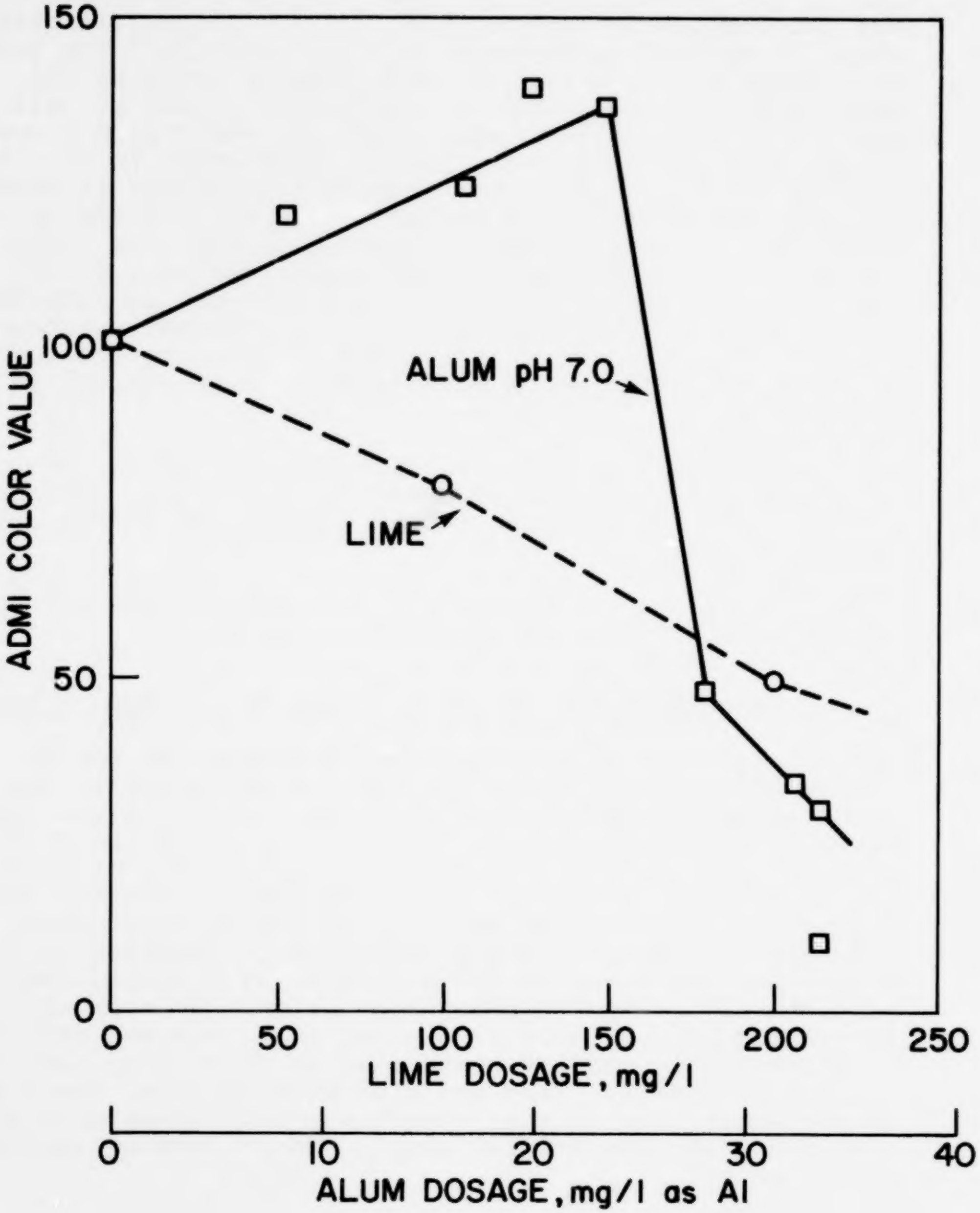

FIGURE 38. Dyeing Wastewater No. 6 (Disperse Dyes on Polyamide Carpet): Color Removal by Lime and Alum Coagulation

an initial apparent enhancement of the color, presumably due to the formation of colloidal aluminum hydroxide which was not completely separated by the Celite prefiltration step, 30 mg/l of aluminum at pH 7.0 decolorized the waste to a value of 50, with increased dosages reducing the color even further. TOC was reduced about 20% by this dosage. Lime effectively decolorized the waste with a dosage of 200 mg/l (pH 11.5) reducing the ADMI color to 50. Addition of the lime turned the samples from orange to pink, but upon readjustment of the pH to 7.6 as required in the ADMI color procedure, the samples converted to a light yellow-green color. No floc were observed as a result of the lime addition but the color was lessened as indicated in the Figure. TOC was only slightly reduced, by about 15-20%. The final BOD_5 of the waste following treatment by 30 mg/l of alum was 6 mg/l, down from an initial value of 78 mg/l.

Two hundred mg/l of Darco HD-3000 decolorized the waste to a value of 65 at pH 8.2 as shown in Figure 39. One thousand mg/l of the powdered carbon reduced the TOC by about 50% to 62 mg/l.

Ozonation of the sample was not investigated due to the very low color value of the raw wastewater.

Dyeing Wastewater No. 7. Acid Chrome Dye on Wool - Exhaust

The color of the acid-chrome dyeing wastewater can be attributed to two components: the mordant black 11 dye and Cr(VI). Measurement of the chromium content of the raw waste by atomic absorption analysis indicated the presence of 37.5 mg/l of total chromium, a good portion of which presumably was in the +VI oxidation state since the dyeing procedure calls for the addition of sodium dichromate. The fact that both lime and alum were ineffective in decolorizing the waste at dosages up to 2000 and 160 mg/l, respectively, supports this presumption; chromium (III) is relatively insoluble at neutral pH values and should have been quite readily coagulated as $Cr(OH)_3$ by the lime or alum treatment. Lime and alum both improved the clarity of the waste (the initial sample was dark brown with some turbidity) but the treated sample had an intense yellow-orange color.

Darco HD-3000 was able to decolorize the waste but only at extremely high dosages as shown in Figure 40. Decolorization was most effective at acidic pH values as shown, with

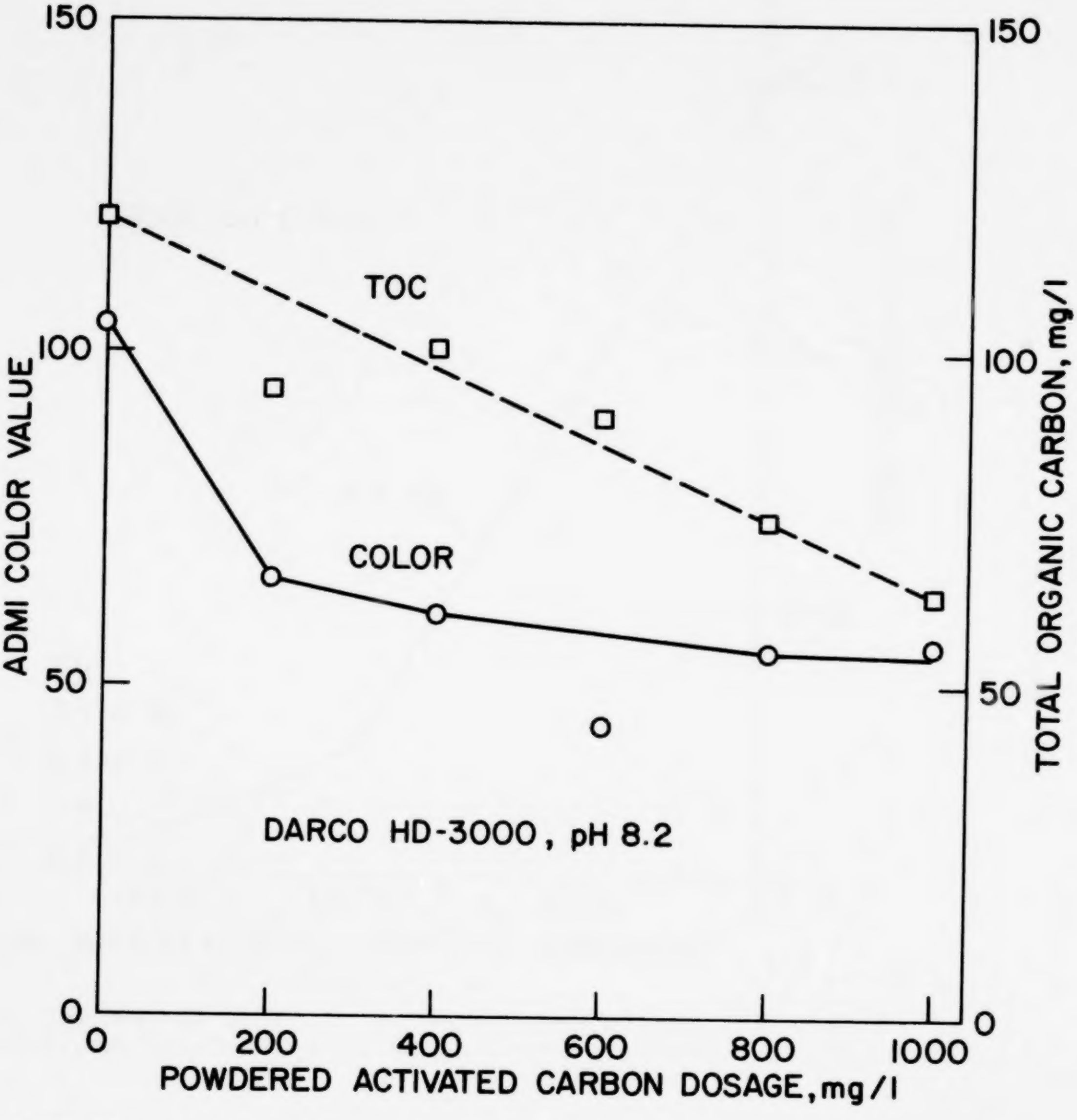

FIGURE 39. Dyeing Wastewater No. 6 (Disperse Dye on Polyamide Carpet): Color and Total Organic Removal by Powdered Activated Carbon

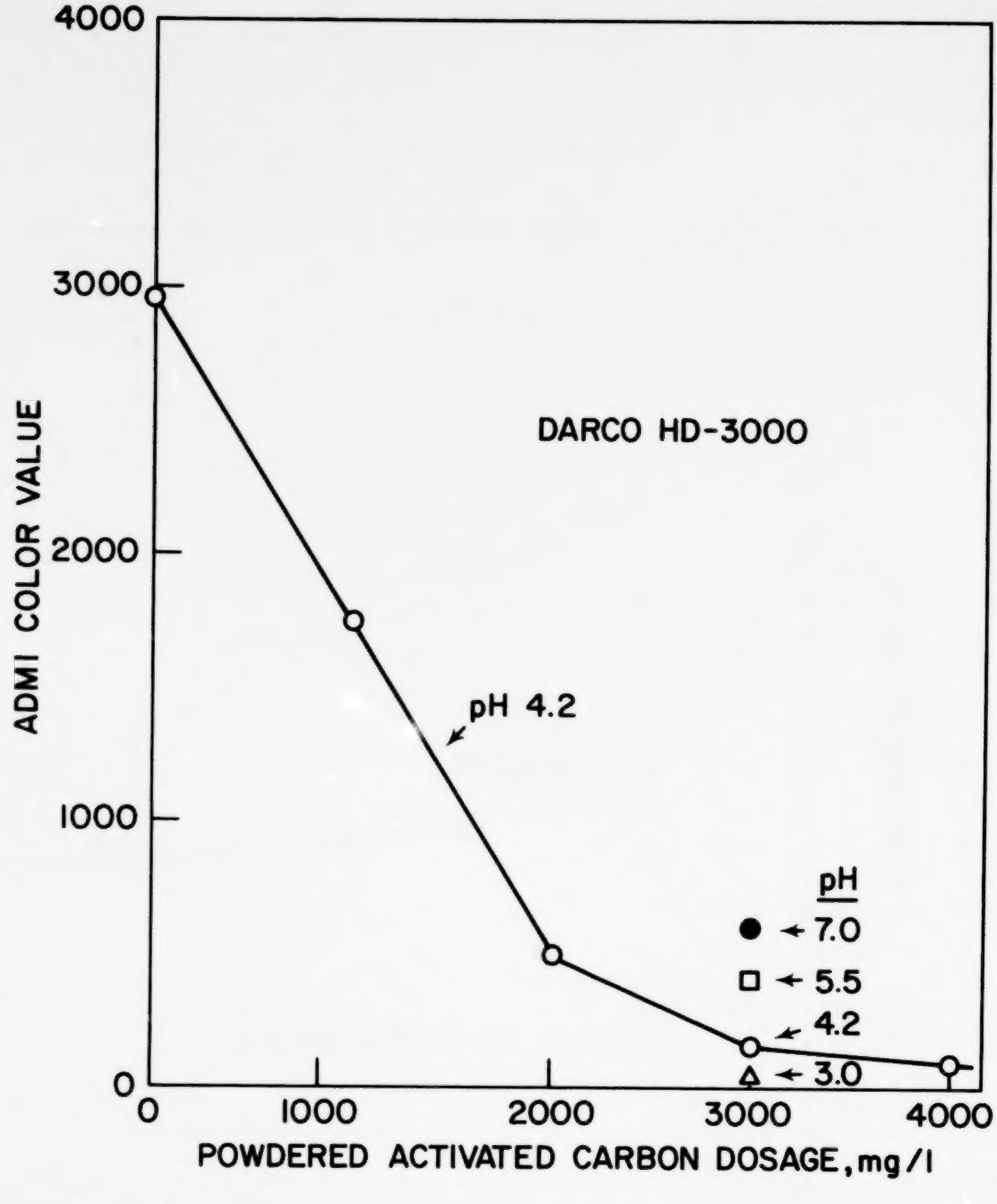

FIGURE 40. Dyeing Wastewater No. 7 (Acid-Chrome Dye on Wool): Decolorization by Powdered Activated Carbon

4 gm/l of HD-3000 at pH 4.2 (the pH of the raw waste) reducing the color to 75. Decolorization was probably a result of reduction of the hexavalent chromium by the activated carbon, the carbon serving as a reducing agent. The residual chromium(III) was either adsorbed and removed on the carbon surface, or precipitated as insoluble chromium hydroxide, $Cr(OH)_3$, and was separated along with the powdered carbon. The mordant black dye was also apparently adsorbed as evidenced by the disappearance of the black color and the low final color value.

Since most of the color of the acid-chrome dyeing wastewater was believed to be due to the residual Cr(VI), application of a reducing agent (ferrous iron) was attempted. The waste was acidified to pH 3 with sulfuric acid and various dosages of Fe(II), as ferrous sulfate, were added. A contact period of 10 minutes was provided between the ferrous iron and the waste at pH 3, after which lime was added to raise the pH to 7 and the treated sample was allowed to settle for 30 min. The residual ADMI color value as a function of added Fe(II) is shown in Figure 41. The optimal dose of about 180 mg/l of Fe(II) corresponds to a theoretical Cr(VI) concentration of approximately 55 mg/l (on the basis of a 3:1 molar stoichiometry of iron to chromium (see Table 51). The residual color was probably due to the mordant black dye and the waste could probably have been decolorized further by the application of activated carbon, but at much lower dosages than given above. The addition of activated carbon prior to reduction of the chromium by ferrous iron is an expensive way of removing Cr(VI). The acidification-reduction-neutralization treatment resulted in a reduction in TOC of about 40% as shown in Figure 42, but BOD was unchanged.

Dyeing Wastewater No. 8. Basic Dye on Polyacrylic - Exhaust

As indicated in Section V, an appreciable amount of the basic dye was removed when the waste was prefiltered by Celite prior to the ADMI color analysis. Consequently, the Celite filtration step was omitted when residual color was measured. Lime and alum resulted in no measurable color reduction at dosages up to 2000 and 315 mg/l, respectively. TOC reduction in both cases was also small.

The basic dye was effectively decolorized by activated carbon adsorption as demonstrated in Figure 43. Various types of powdered carbon were investigated, and the effect of pH was also examined. Table 52 shows the effect of pH

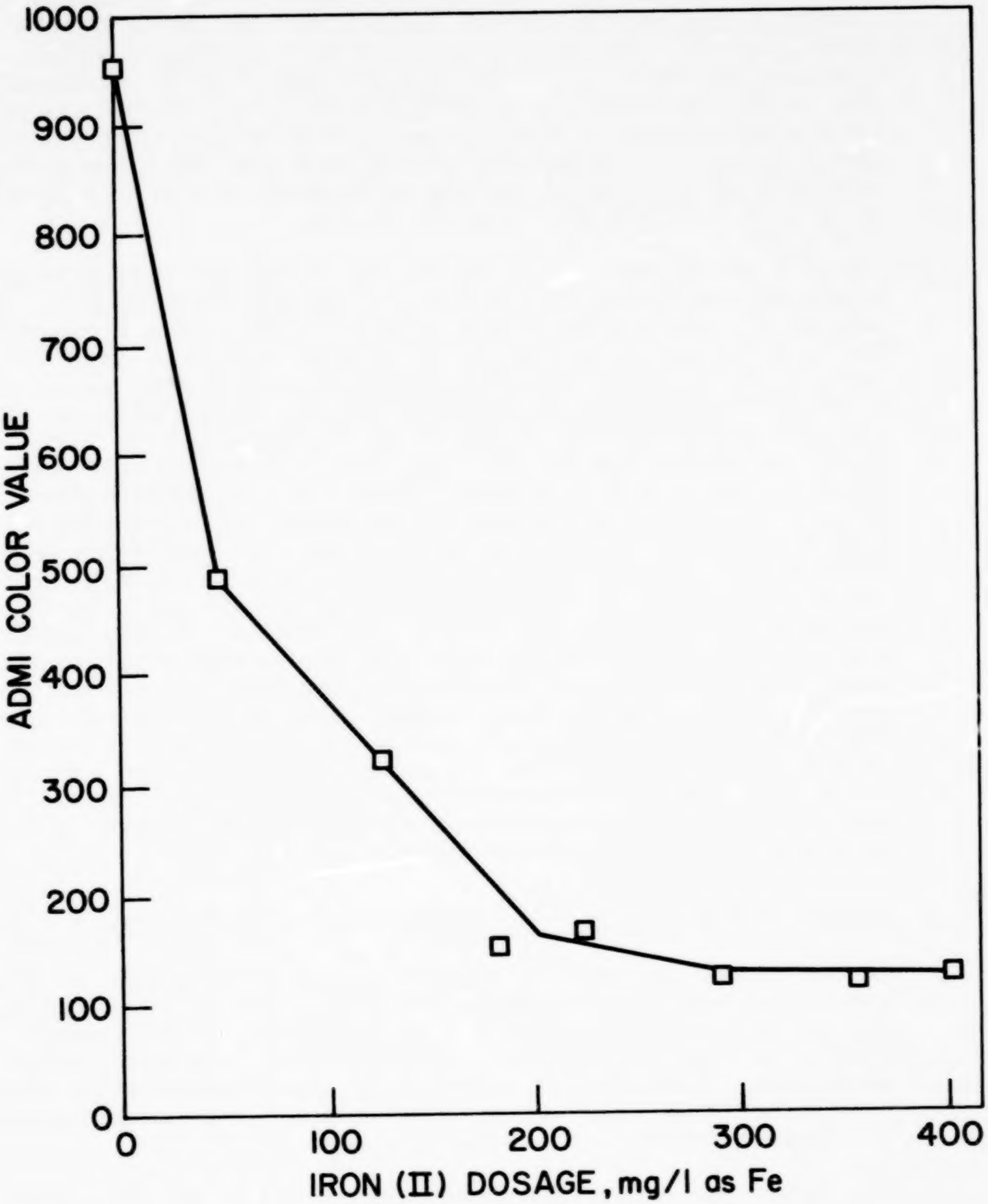

FIGURE 41. Dyeing Wastewater No. 7 (Acid-Chrome Dye on Wool): Removal of Color by Acidification, Iron(II) Reduction, Neutralization

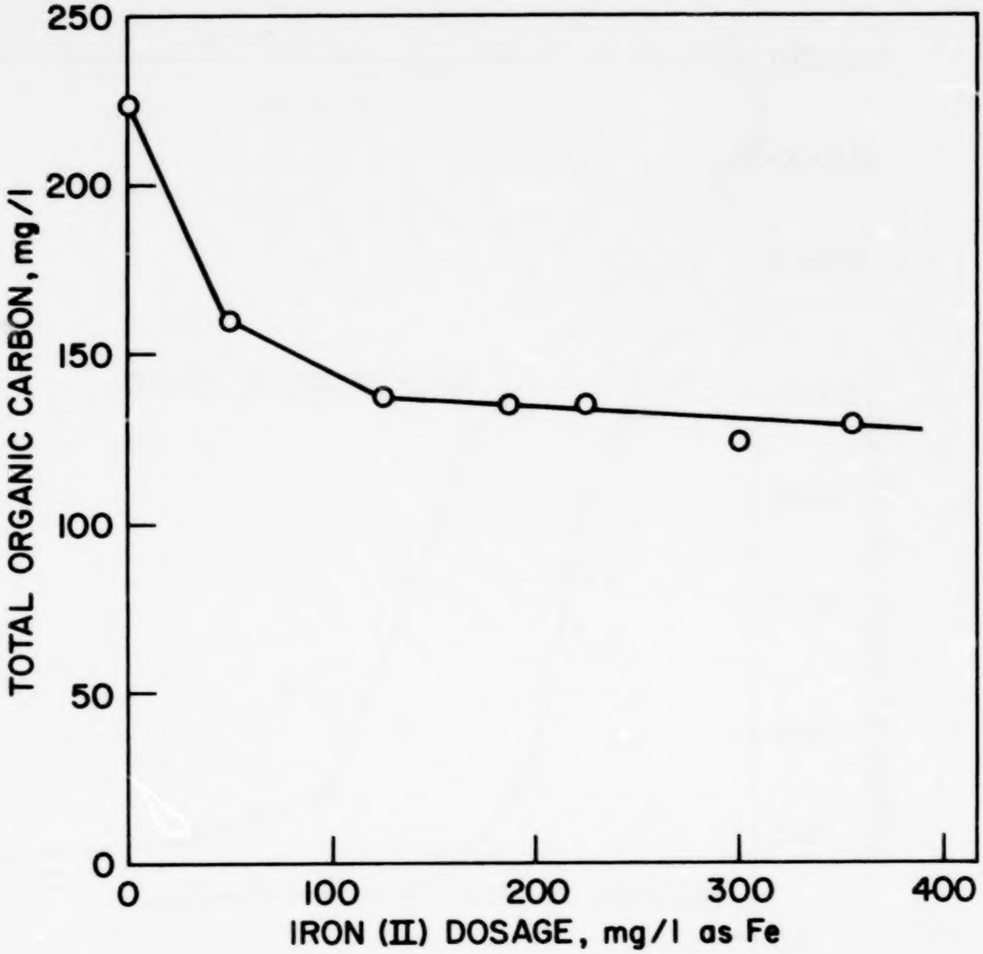

FIGURE 42. Dyeing Wastewater No. 7 (Acid-Chrome Dye on Wool): Total Organic Carbon Removal by Acidification, Iron(II) Addition, Neutralization

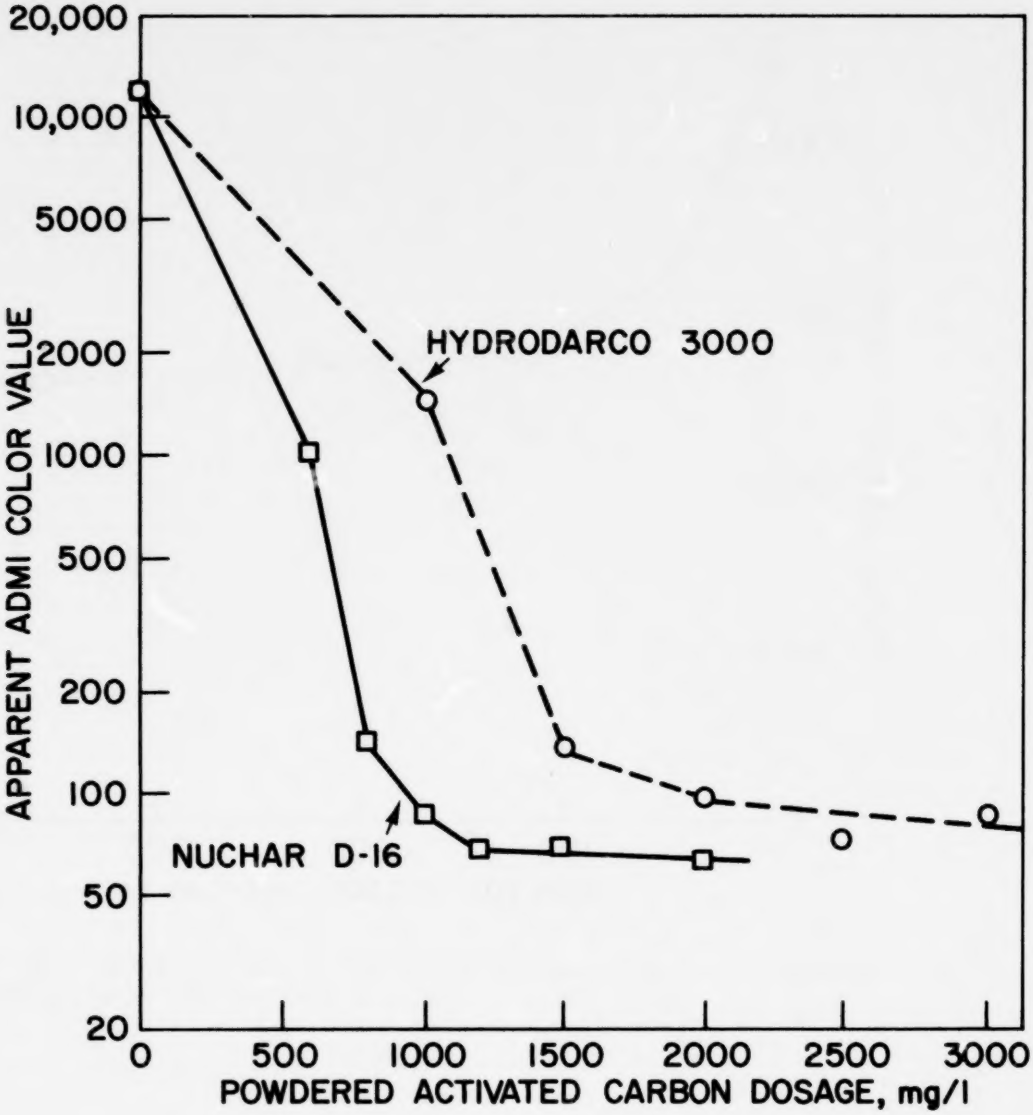

FIGURE 43. Dyeing Wastewater No. 8 (Basic Dye on Polyacrylic): Decolorization by Powdered Activated Carbon

TABLE 51. EFFECT OF IRON(II) REDUCTION[a] ON DYEING WASTEWATER NO. 7 (ACID-CHROME DYE)

Fe(II) dosage, mg/l	Theoretical Cr(VI) reduced, mg/l	ADMI color value
0	0	948
49	15	488
126	39	322
184	57	144
224	69	166
290	89	123
360	111	120
405	125	128

[a] Wastewater was acidified to pH 3 with H_2SO_4, treated with Fe(II), neutralized with lime, and settled.

on decolorization of the waste by 1500 mg/l of Darco HD-3000; it is apparent that pH 4.5 (the initial pH of the raw waste) is most effective for decolorization. Table 53 shows the effect of different grades of powdered carbon at applied dosages of 1500 mg/l and pH 4.5. The two Nuchar grades and Darco KB are seen to be equally effective in decolorizing the waste sample. Figure 43 shows the reduction in apparent ADMI color as a function of carbon dosage for the Nuchar D-16 and Darco HD-3000 at pH 4.5; 1000 mg/l of the Nuchar reduced the color to less than 100. Presumably the same degree of treatment could be achieved with Darco KB in accordance with the results in Table 53. TOC removal by 1000 mg/l of Nuchar D-16 was about 40% as shown in Figure 44. BOD removal was approximately 30%.

Decolorization of the basic dyeing wastewater by ozone is shown in Figure 45. Ozonation resulted in a reduction in pH of the waste. Despite the lower partial pressure of ozone in the more acidic sample, ozone is more efficient in decolorizing the waste at the lower pH. This was apparently due to the longer lag exhibited by the pH 7.6 sample. (A lag was not observed for the pH 4.1 sample, but this

TABLE 52. EFFECT OF pH ON TREATMENT OF DYEING WASTEWATER NO. 8 (BASIC DYE ON POLYACRYLIC) BY POWDERED ACTIVATED CARBON

Dosage of DARCO HD-3000, mg/l	pH	TOC, mg/l	Apparent ADMI color value
1500	2.0	148	204
1500	2.7	144	205
1500	3.7	134	202
1500	4.5	134	141
1500	5	138	186
1500	6	144	212

TABLE 53. EFFECT OF DIFFERENT TYPES OF POWDERED ACTIVATED CARBONS ON TREATMENT OF DYEING WASTEWATER NO. 8 (BASIC DYE ON POLYACRYLIC) AT pH 4.5

Type of powdered carbon	Dosage, mg/l	pH	TOC, mg/l	Apparent ADMI color value
DARCO HDB	1500	4.5	132	147
DARCO S-51	1500	4.5	142	207
DARCO KB	1500	4.5	108	66
DARCO HD-3000	1500	4.5	140	153
NUCHAR D-14	1500	4.5	134	62
NUCHAR D-16	1500	4.5	125	76

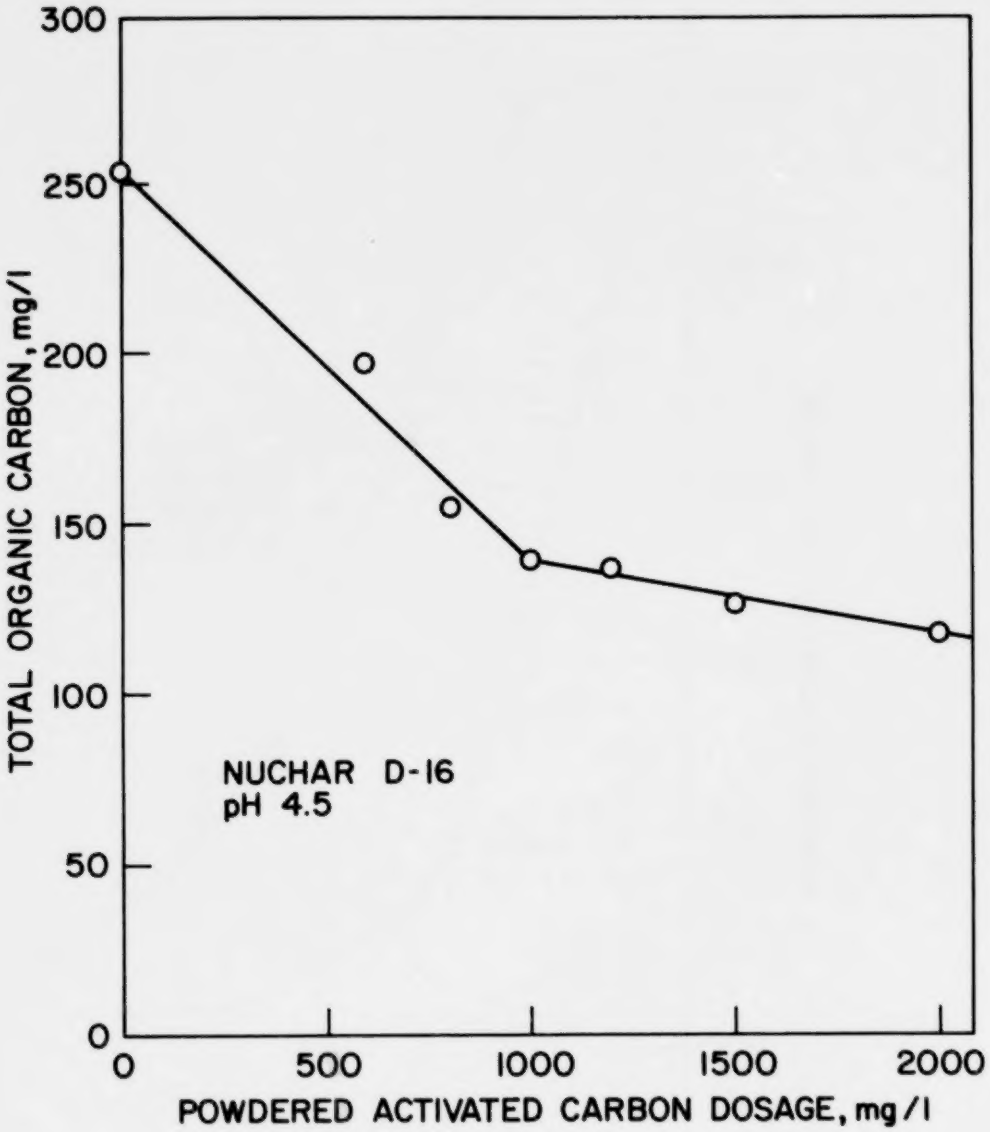

FIGURE 44. Dyeing Wastewater No. 8 (Basic Dye on Polyacrylic): Total Organic Carbon Removal by Powdered Activated Carbon

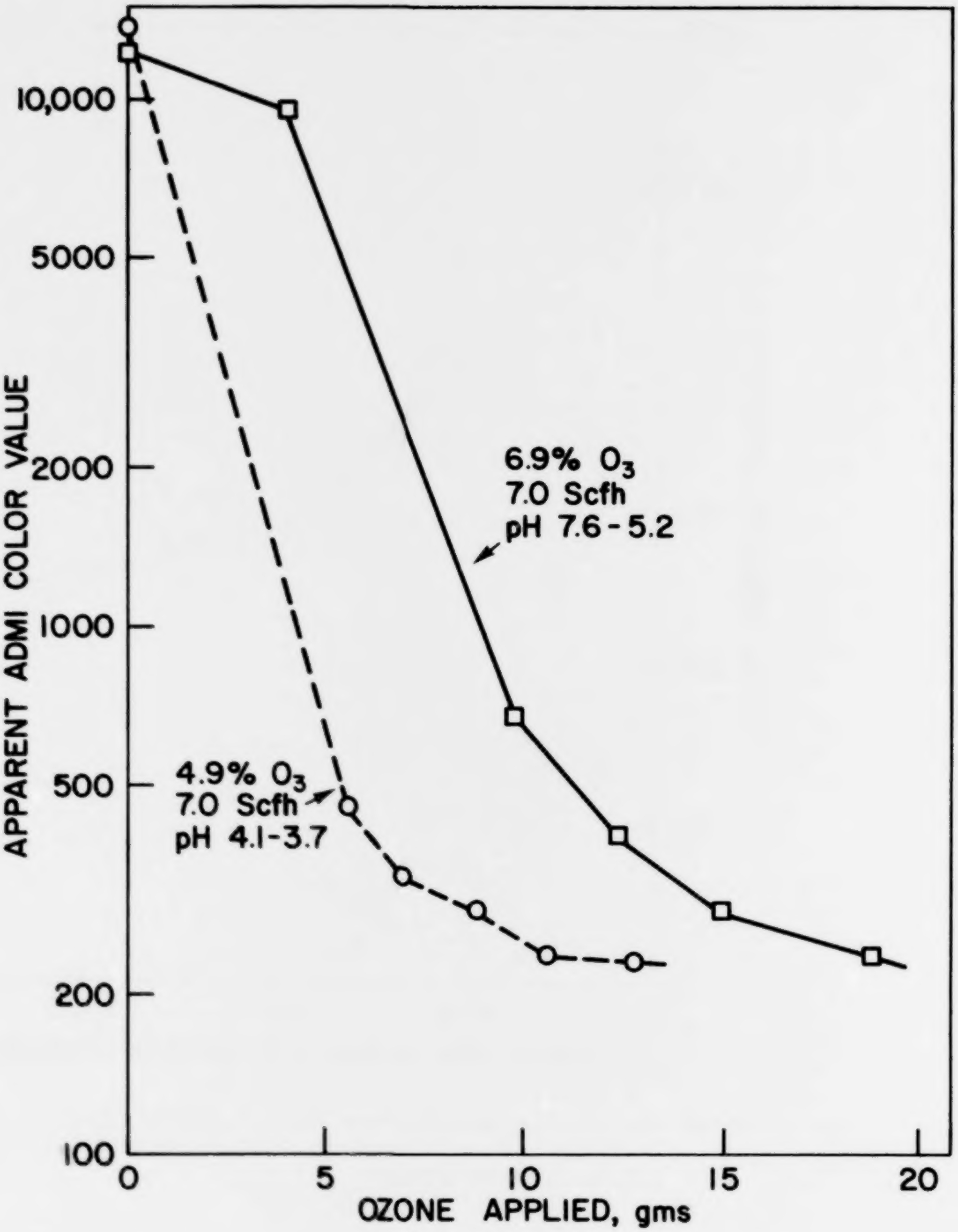

FIGURE 45. Dyeing Wastewater No. 8 (Basic Dye on Polyacrylic): Decolorization by Ozone

may have been due to the relatively long interval before the first aliquot was removed.) Decolorization was quite effective, with the color reduced from 12,000 to 500 by the application of 6 gms of ozone (1 gm/l), but the apparent color could not be reduced below 200. There was no reduction in the TOC of the waste as a result of ozonation, but the BOD_5 was observed to increase from 160 to 270 mg/l.

Dyeing Wastewater No. 9. Disperse Dyes on Polyester Carpet - Exhaust

This waste was highly turbid (suspended solids concentration of 101 mg/l) and filtration of the samples was required prior to the color analyses. However, to avoid a significant loss in color as a result of adsorption by Celite, the treated samples were simply filtered through Reeve-Angel paper to eliminate the turbidity without affecting the apparent color of the aliquots. The ADMI color analysis was performed on these prefiltered samples.

Lime and alum effectively coagulated the disperse dyeing wastewater as shown in Figure 46; 1000 mg/l of lime (pH 11.9) reduced the apparent color to 132. In the case of alum, initial enhancement of the apparent "color" was measured, presumably due to the formation of colloidal aluminum hydroxide which was not satisfactorily removed by the Reeve-Angel prefiltration. At higher doses, however, alum proved to be an effective coagulant for this waste, with a dosage of 150 mg/l of Al reducing the apparent color to 80. pH 5 again was more effective for alum coagulation than pH 7. At the lower alum doses, the aluminum hydroxide floc settled rather poorly but at dosages of 125 and 150 mg/l good-settling floc resulted. TOC removal by alum was good with reductions of about 60% resulting from the application of 160 mg/l of aluminum at pH 5 (see Figure 47). TOC removal by lime was about 20%. The final BOD_5 after treatment with 160 mg/l of Al(III) at pH 5 was 60 mg/l, a reduction of about 65%.

Nuchar D-16, at dosages up to 2000 mg/l, at pH 7.1, gave no measurable reduction in color. TOC, however, was reduced approximately 70% by 2000 mg/l of the Nuchar carbon.

Decolorization of the disperse dyeing wastewater by ozone is shown in Figure 48. Under conditions of neutral pH, a lag was observed after which 24 gms of ozone (4 gms/l) was required to decolorize the waste to less than 100. Under acidic conditions, only 15 gms (2.5 gms/l) was able to

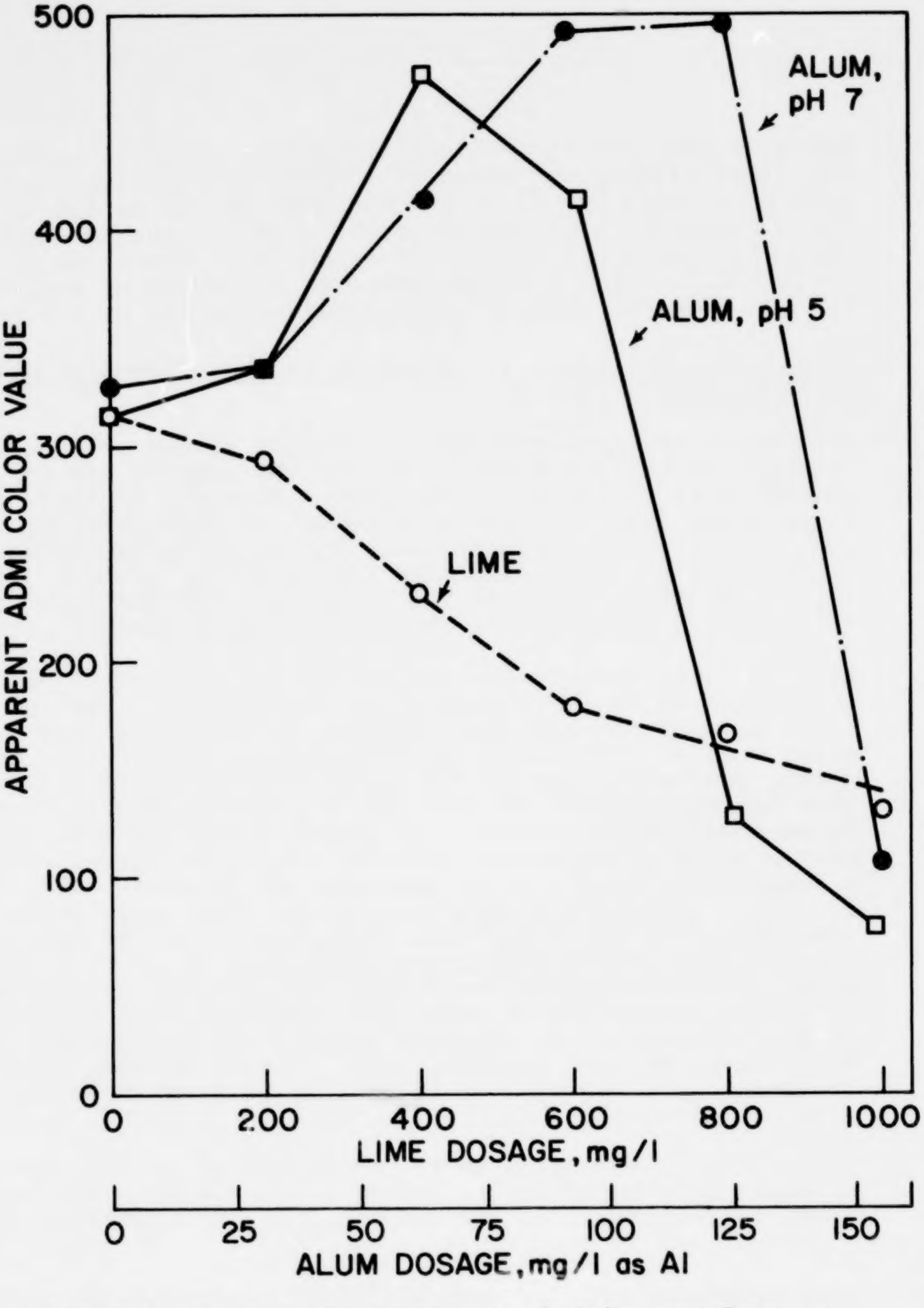

FIGURE 46. Dyeing Wastewater No. 9 (Disperse Dyes on Polyester Carpet): Color Removal by Lime and Alum Coagulation

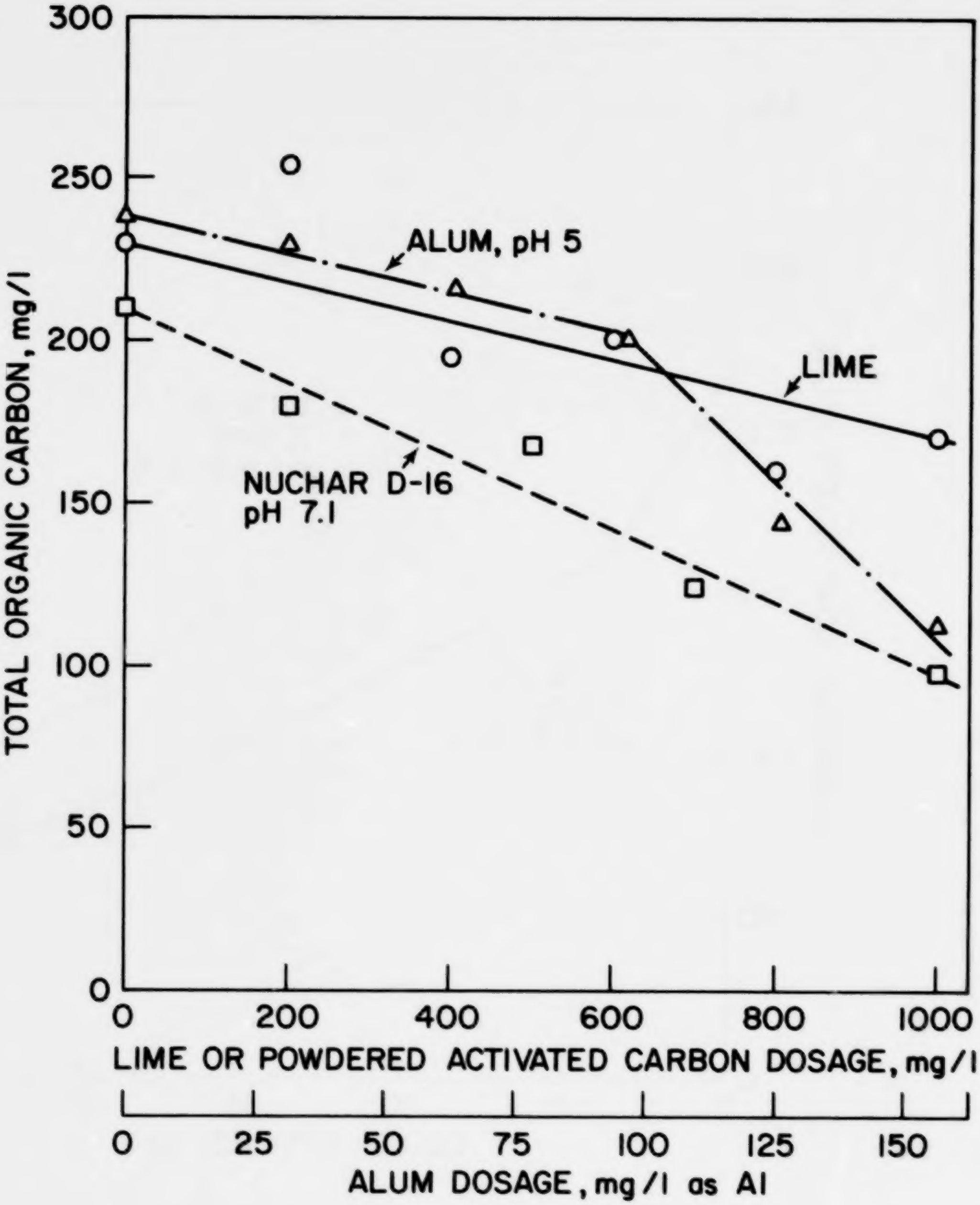

FIGURE 47. Dyeing Wastewater No. 9 (Disperse Dyes on Polyester Carpet): Removal of Total Organic Carbon by Lime, Alum and Powdered Activated Carbon

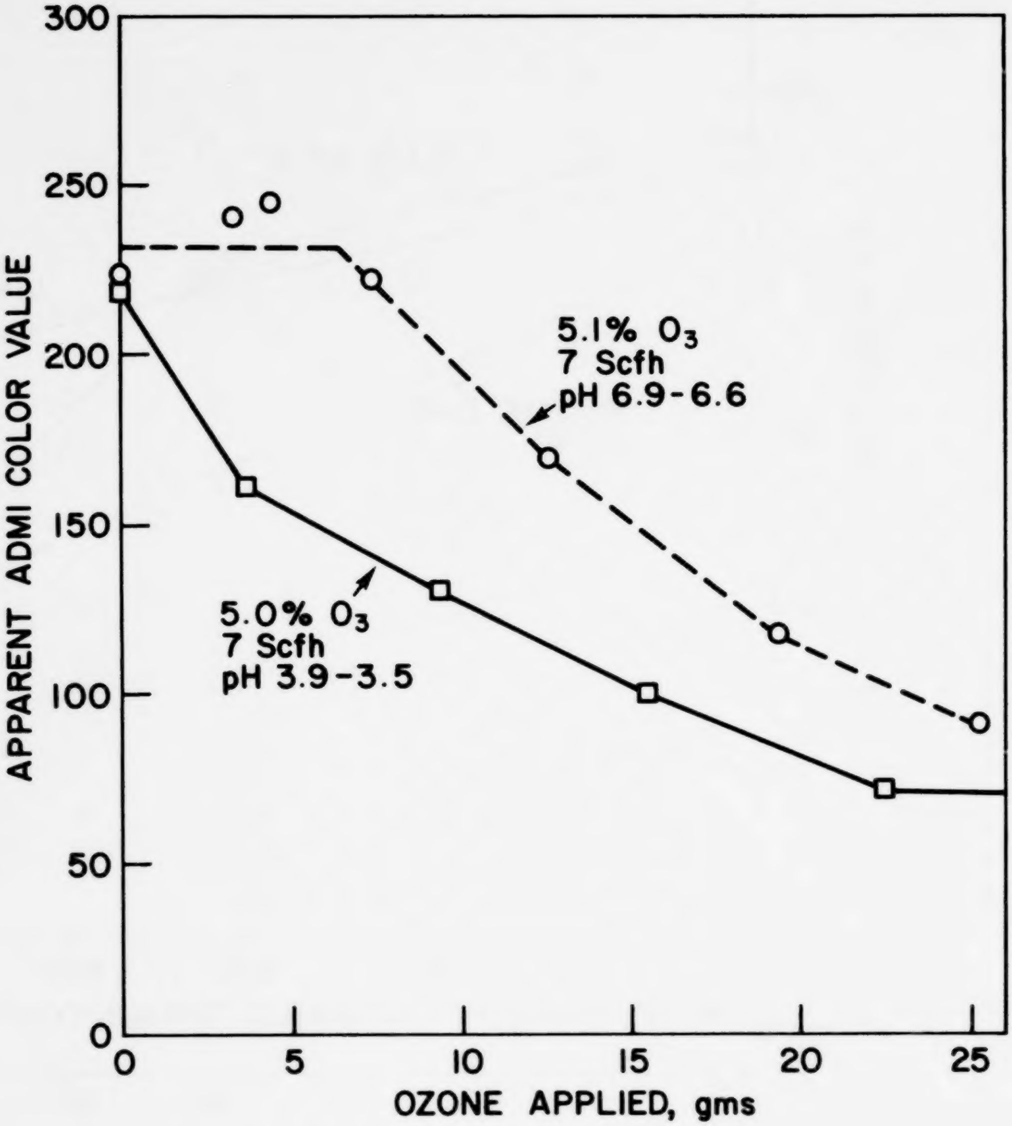

FIGURE 48. Dyeing Wastewater No. 9 (Disperse Dyes on Polyester Carpet): Decolorization by Ozone

achieve the same degree of decolorization. No change in TOC was measured but, again, the BOD_5 increased as a result of ozonation from an initial concentration of 80 mg/l to a final concentration for both samples of approximately 105 mg/l. (It should be noted that the initial concentrations of TOC and BOD_5, and the initial color of dyeing wastewater no. 9 immediately prior to ozone treatment were somewhat less than the initial values of the fresh waste. Apparently a change in the composition of the waste had taken place during storage.)

Dyeing Wastewater No. 10. Acid Dye on Polyamide - Exhaust

Alum and lime were relatively ineffective in decolorizing the acid dye. Alum, at pH 7, at doses up to 160 mg/l of Al reduced the ADMI color from 4000 to 2150 and the TOC from 315 to 160 mg/l as shown in Figure 49. Lime provided a similar degree of decolorization to 2140 at a dosage of 1000 mg/l (pH 11.8) but no apparent formation of floc was observed. In the case of lime, decolorization was apparently due to a complexation effect which altered the color of the sample. There was no removal of TOC with 1000 mg/l of lime. By comparison, alum resulted in a good-settling floc, but decolorization was still not very effective.

Table 54 shows the effect of 1000 mg/l of Darco HD-3000 on the acid dyeing wastewater at various pH values, showing that pH 5.1 (the initial pH of the waste) was most effective for decolorizing the waste. Table 55 shows the effect of 900 mg/l of several different grades of powdered carbon on the color of the waste at pH 5.1. Darco HDB and KB, and Nuchar D-14 and D-16 were significantly more effective than Darco HD-3000. Figure 50 shows the effect of different doses of three types of carbons on the color of the acid dyeing wastewater. Decolorization was fairly effective, with 1000 mg/l of all three carbons reducing the color of the waste to about 260. Increasing doses, however, brought about very little additional decolorization, with the color leveling off at approximately 200. The TOC was reduced approximately 35% by the application of 1000 mg/l of Darco KB as shown in Figure 51; KB was more effective than HD-3000. The BOD_5 was also reduced approximately 35% to a final value of 150 mg/l. Figure 85a and the companion Table 67 (presented at the end of this section) shows the appearance of the acid dyeing wastewater after various doses of Darco HD-3000. The blue color appears to be essentially removed by about 1000 to 1200 mg/l of carbon, but the residual greyish color appears to be resistant to subsequent decolorization by additional doses of carbon.

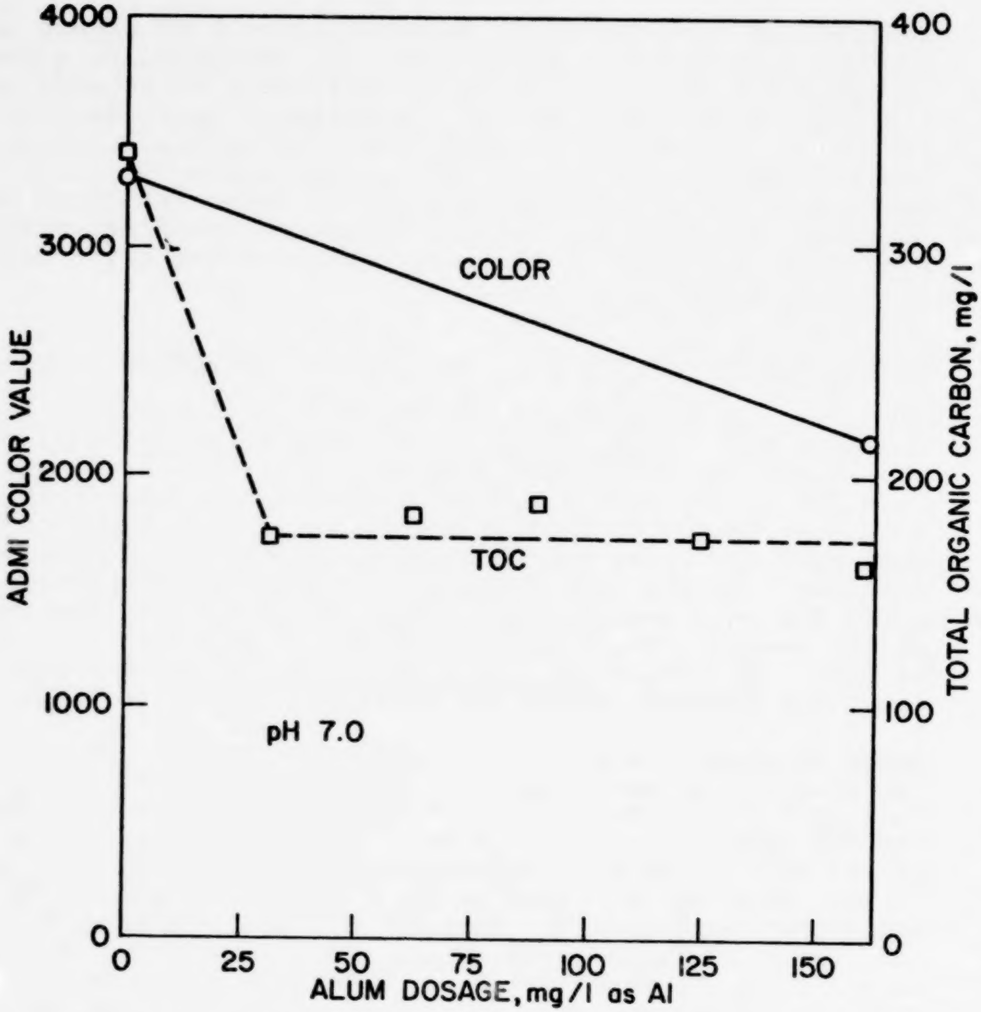

FIGURE 49. Dyeing Wastewater No. 10 (Acid Dye on Polyamide): Color and Total Organic Carbon Removal by Alum Coagulation

TABLE 54. EFFECT OF pH ON TREATMENT OF DYEING WASTEWATER NO. 10 (ACID DYE ON POLYAMIDE) BY POWDERED ACTIVATED CARBON

Dosage of DARCO HD-3000, mg/l	pH	TOC, mg/l	ADMI color value
1000	2	196	322
1000	2.3	178	329
1000	3.8	182	306
1000	5.1	208	270
1000	6.0	246	425

TABLE 55. EFFECT OF DIFFERENT TYPES OF POWDERED ACTIVATED CARBONS ON TREATMENT OF DYEING WASTEWATER NO. 10 (ACID DYE ON POLYAMIDE) AT pH 5.1

Type of powdered carbon	Dosage, mg/l	pH	ADMI color value
DARCO HD-3000	900	5.1	649
DARCO HDB	900	5.1	312
DARCO KB	900	5.1	338
NUCHAR D-14	900	5.1	227
NUCHAR D-16	900	5.1	298

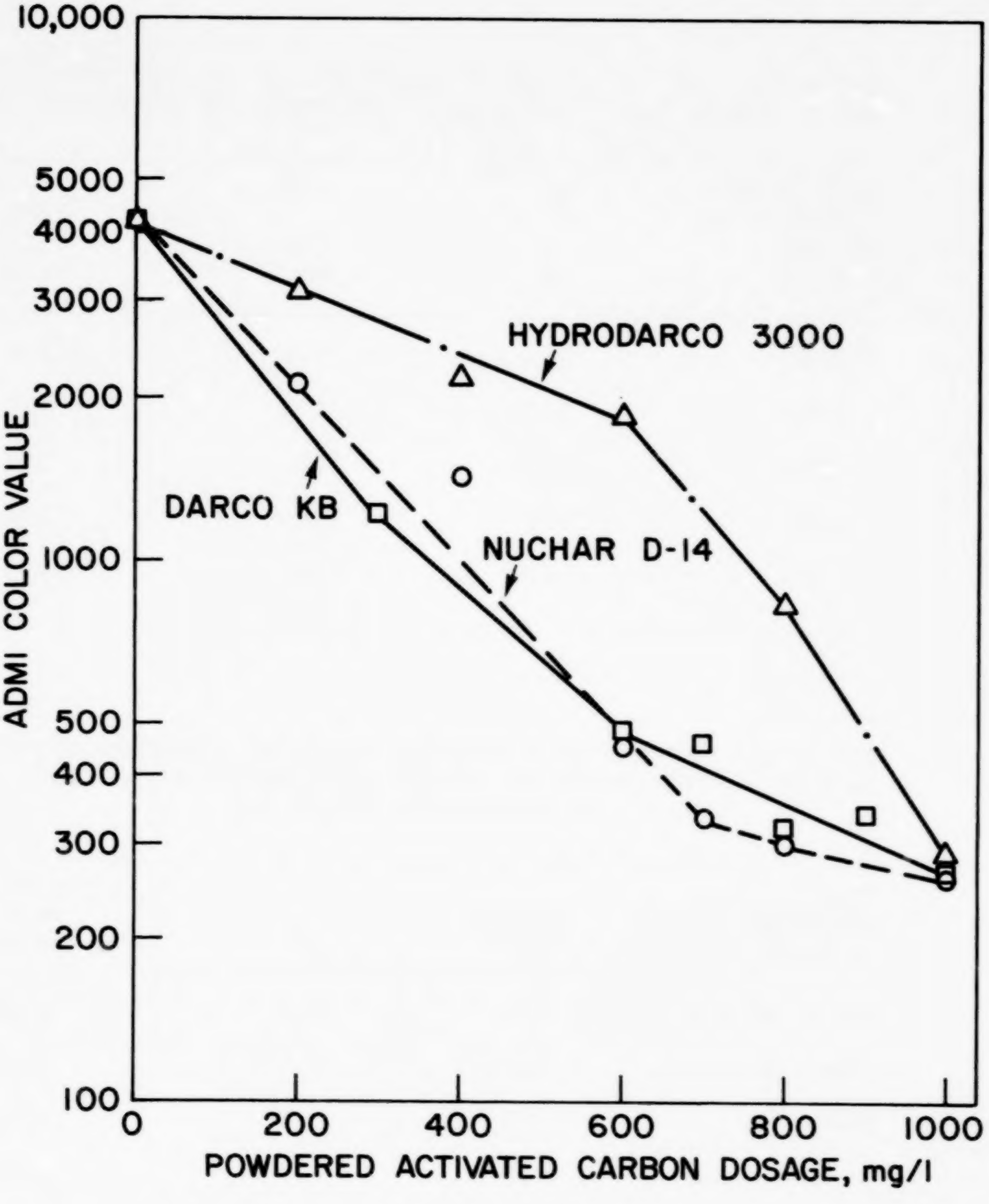

FIGURE 50. Dyeing Wastewater No. 10 (Acid Dye on Polyamide): Decolorization by Powdered Activated Carbon

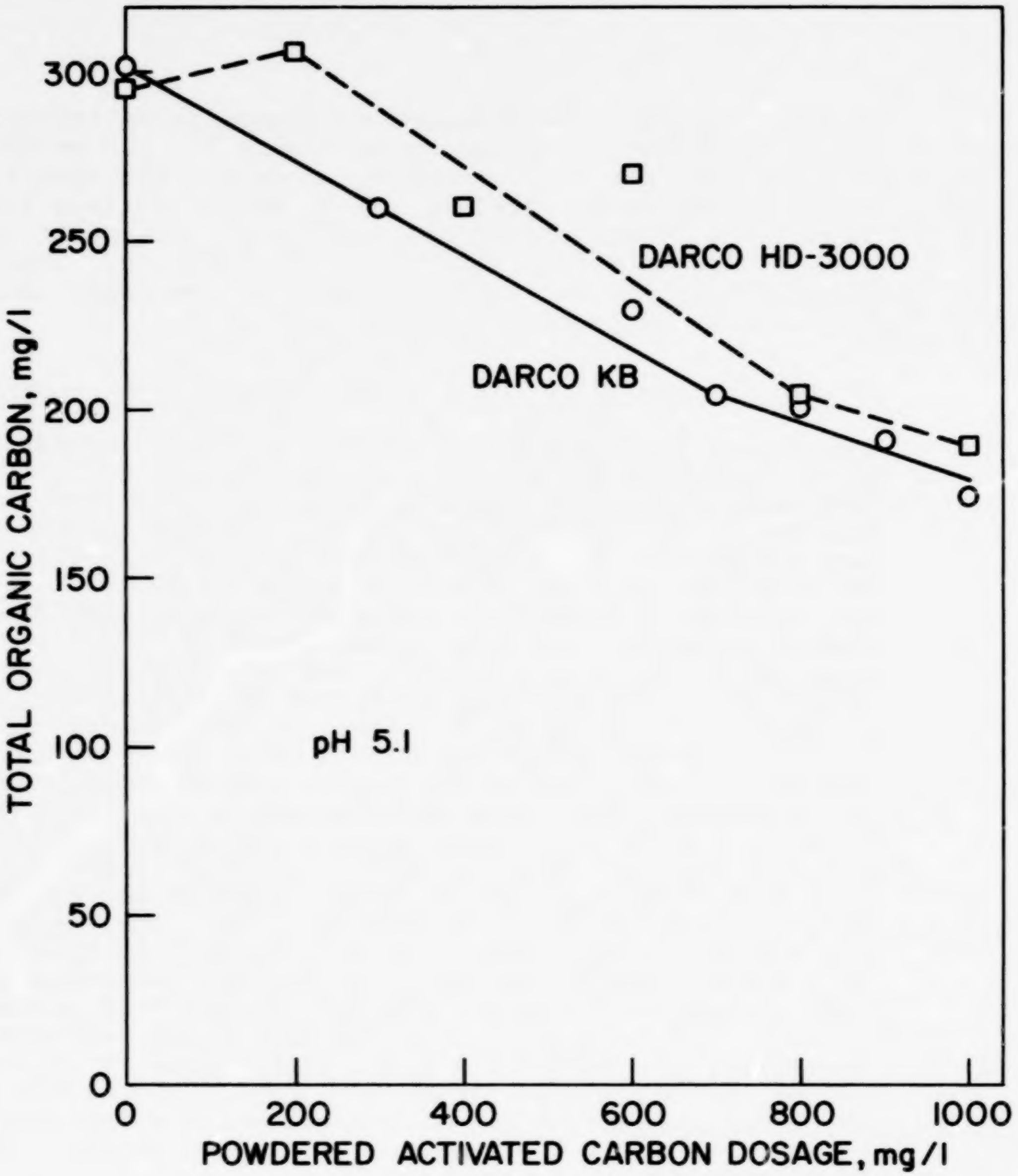

FIGURE 51. Dyeing Wastewater No. 10 (Acid Dye on Polyamide): Removal of Total Organic Carbon by Powdered Activated Carbon

Similar results were observed by ozonation of the acid dyeing wastewater. As shown in Figure 52, the waste is decolorized to a fair extent by ozone but the reduction in color seemed to be leveling off at about 400 (see also Figure 85b at the end of this section). The pH of the sample decreased from 6.6 to 3.5 by ozonation. There was no change in TOC but again the BOD_5 of the waste increased as a result of ozone treatment.

Dyeing Wastewater No. 11. Direct Dye on Rayon - Exhaust

The direct black dyeing wastewater was very intensely colored as reflected by the initial color value of 12,500. Lime was ineffective, with no apparent color removal at dosages up to 3000 mg/l (pH 12.3). The TOC concentration was reduced by 25% by this dosage of lime. Al(III) decreased the color to 2000 at a dosage of 30 mg/l at pH 5, but further alum addition resulted in no further decolorization as shown in Figure 53 and Table 56. Following alum treatment, the sample appeared red in color as shown in Figure 85c. TOC was reduced by the 30 mg/l application of aluminum to 27 mg/l, in effect an 80% reduction from the initial TOC value (see Figure 54). Powdered activated carbon by itself was ineffective in decolorizing the waste or in removing TOC, with applications of 2000 mg/l of Nuchar D-14 at a pH of 6.6 resulting in no measurable reduction in color or TOC. However, when activated carbon was coupled with alum coagulation, decolorization was quite effective as shown in Figure 53 and Table 56. The direct dyeing wastewater was coagulated with 30 mg/l of aluminum at pH 5 and allowed to settle. The residual supernatant was then treated with various doses of Nuchar D-14 powdered carbon. Six hundred mg/l of the carbon was sufficient to decolorize the waste to a final color value of 34 and to reduce the TOC concentration to 3 mg/l. Figure 85c shows the effectiveness of the alum treatment coupled with the subsequent addition of powdered activated carbon. The final BOD_5 was less than 1 mg/l.

Ozonation was relatively ineffective in decolorizing the direct dyeing wastewater. Although the color was substantially reduced by ozone (see Figure 55), the application of 28 gms of ozone (about 4.5 gms/l) still left a residual color greater than 1100. The reaction was somewhat faster when the pH was elevated by the addition of a base, but ozonation caused the pH to decrease significantly. Figure 85d shows the colors of the samples at various stages of the ozone treatment. TOC was reduced slightly to 130 mg/l but the BOD_5 increased.

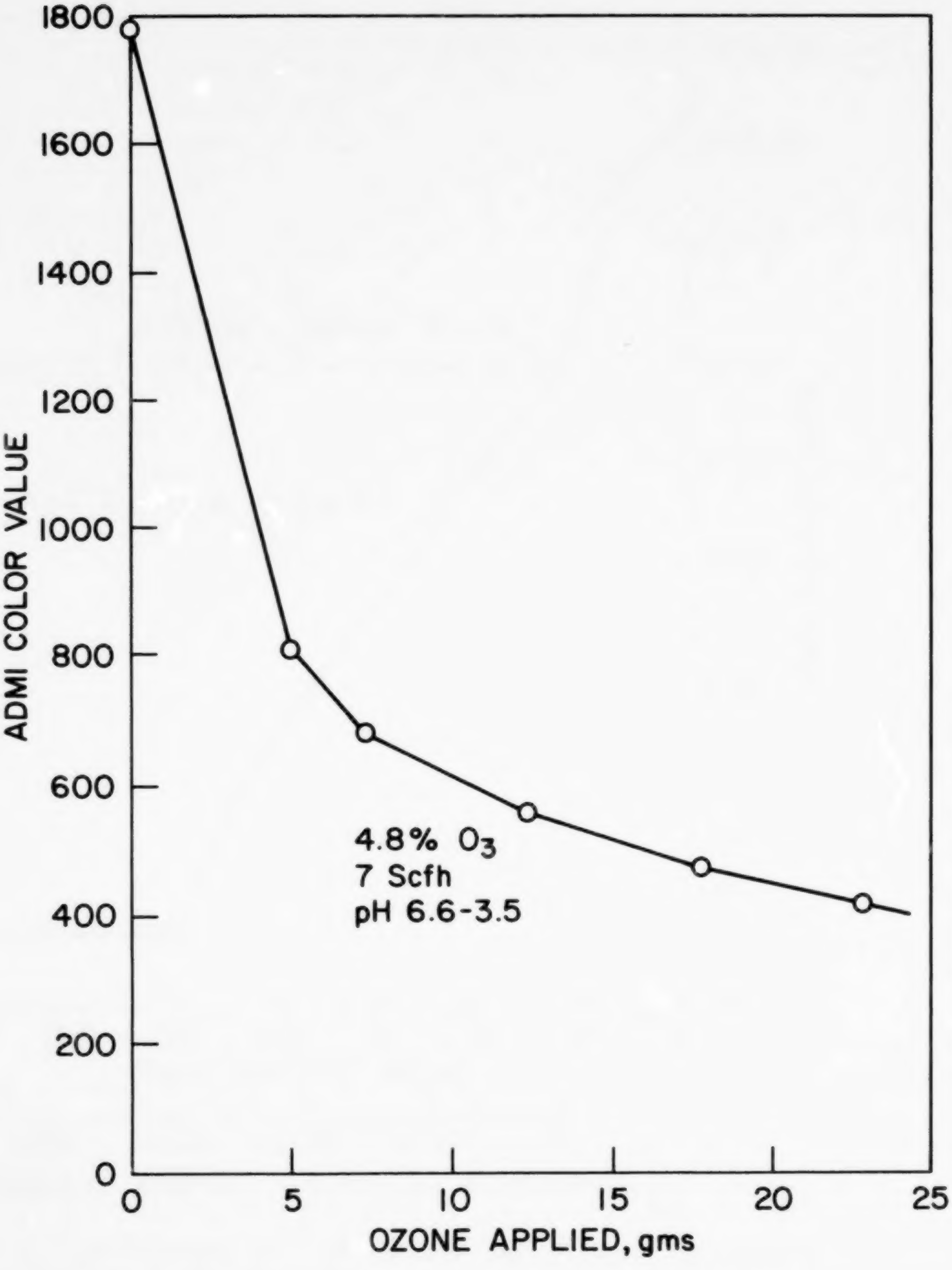

FIGURE 52. Dyeing Wastewater No. 10 (Acid Dye on Polyamide): Decolorization by Ozone

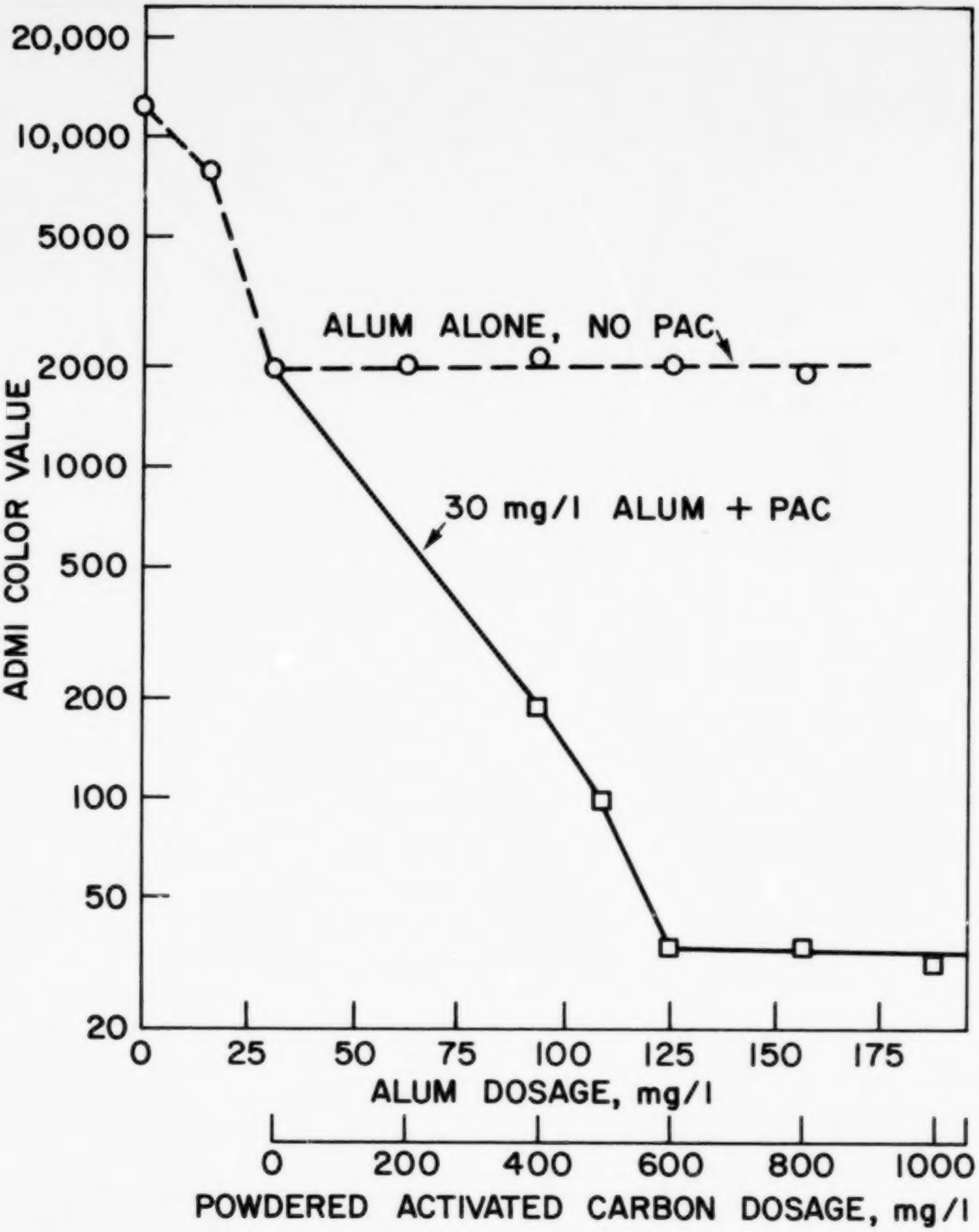

FIGURE 53. Dyeing Wastewater No. 11 (Direct Dye on Rayon): Decolorization by Alum Coagulation Alone and by Two-Stage Sequence Involving Alum Coagulation and Powdered Activated Carbon Adsorption

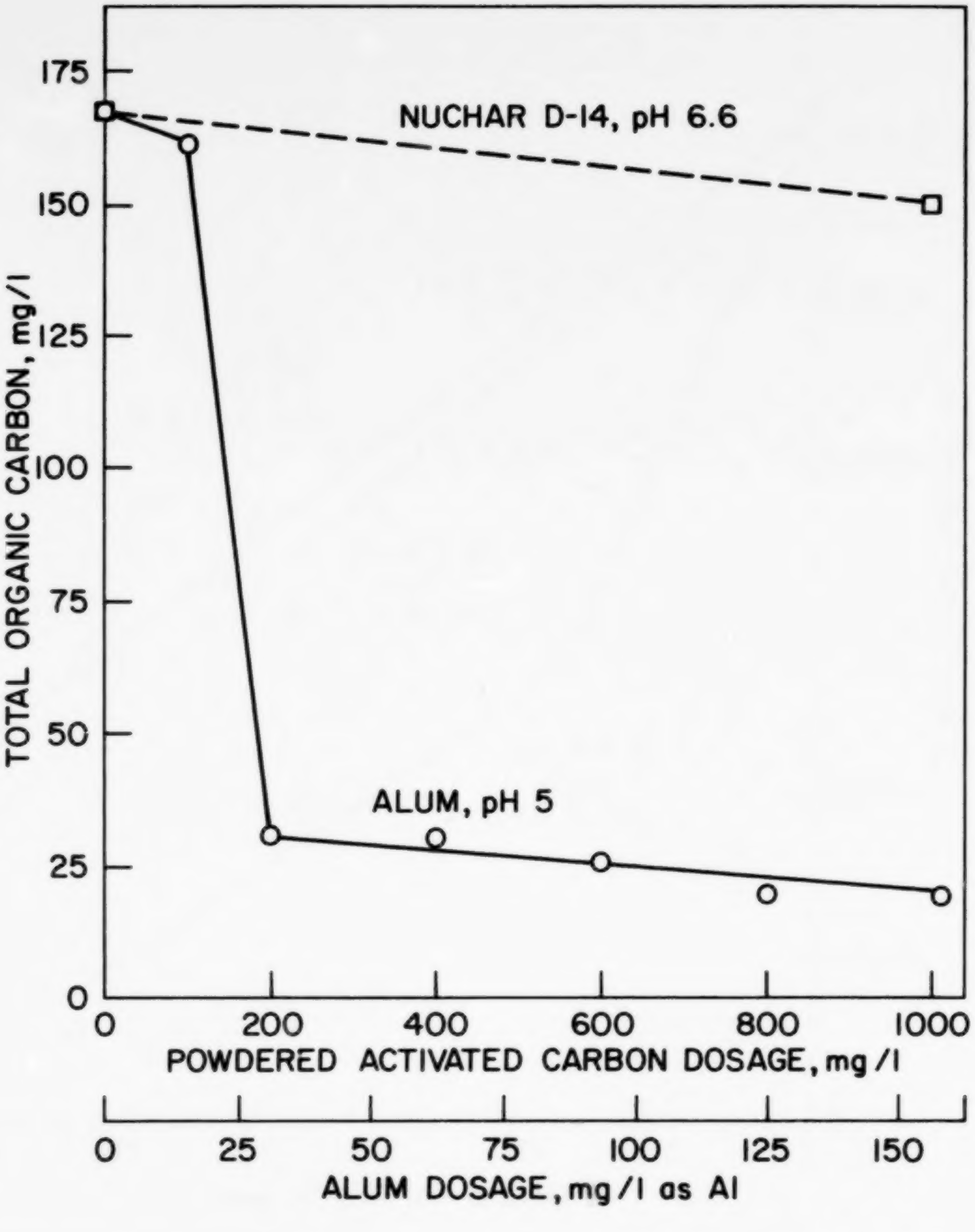

FIGURE 54. Dyeing Wastewater No. 11 (Direct Dye on Rayon): Removal of Total Organic Carbon by Alum Coagulation or Powdered Activated Carbon Adsorption

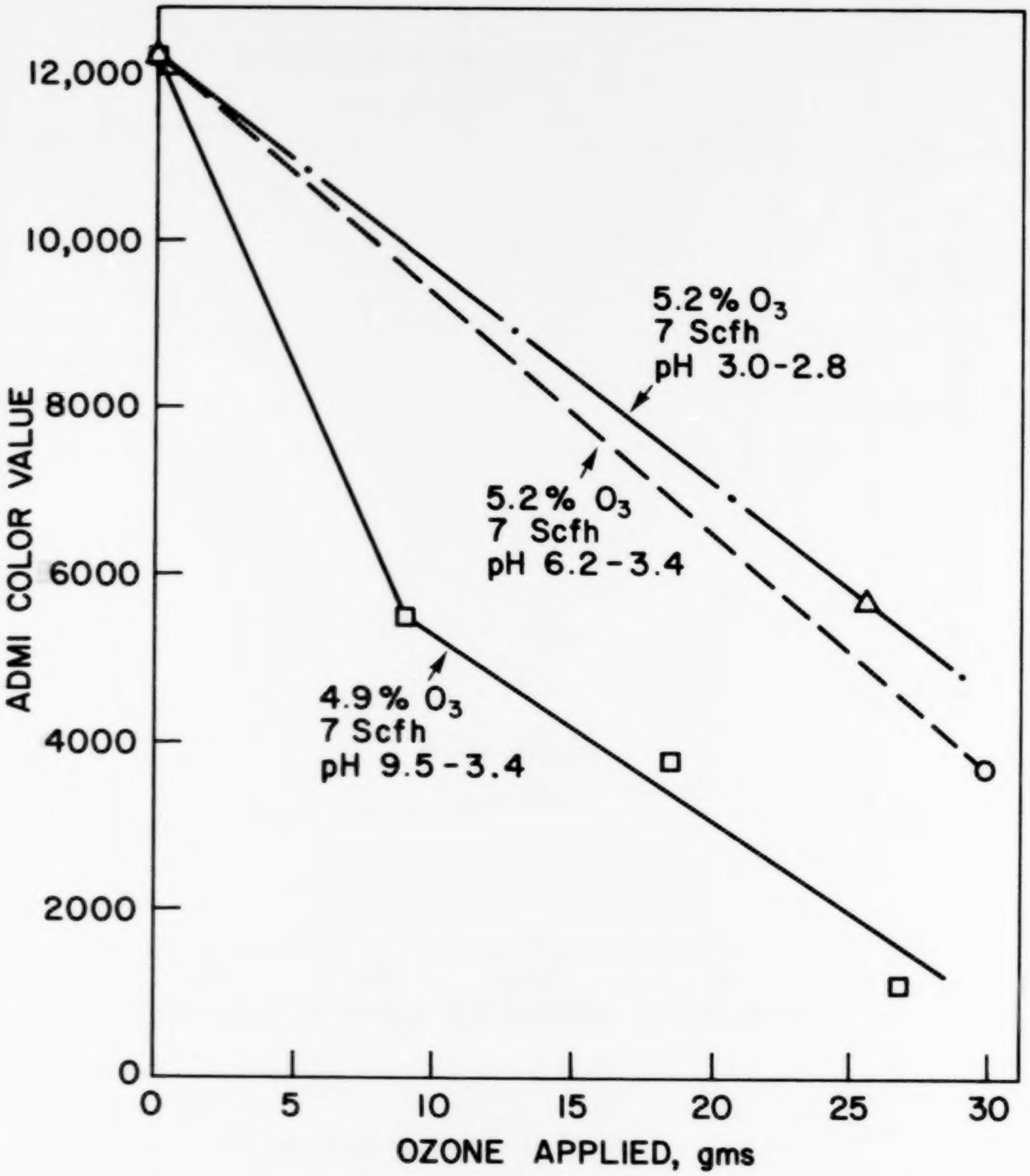

FIGURE 55. Dyeing Wastewater No. 11 (Direct Dye on Rayon): Decolorization by Ozone

TABLE 56. EFFECT OF ALUM AND POWDERED ACTIVATED CARBON ON TREATMENT OF DYEING WASTEWATER NO. 11 (DIRECT DYE ON RAYON)

Al(III) dosage, mg/l	PAC[a] dosage, mg/l	pH	TOC, mg/l	ADMI color
0	0	6.6	171	11,050
16	0	5.0	159	7,920
32	0	5.0	27	1,975
64	0	5.0	28	2,029
32	0	5.0	27	1,975
32	400	5.0	7	186
32	500	5.0	---	97
32	600	5.0	3	34
0	2000	6.6	148	10,915

[a] NUCHAR D-14

Dyeing Wastewater No. 12. Direct Developed Dye on Rayon - Exhaust

Coagulation of the direct developed dyeing wastewater with alum provided a significant degree of decolorization at low doses, but higher doses had no additional effect on color removal as shown in Figure 56 and Table 57. Alum at pH 5 was more effective than at pH 7, but the color could not be reduced below 300 by Al(III). Similar results were observed with lime as shown in Figure 57, with 400 mg/l (pH 11.8) reducing the color to 300 below which no further appreciable decolorization occurred. It should be noted that the addition of lime resulted in a floc which settled poorly. The application of powdered activated carbon (Nuchar D-14) at doses up to 1000 mg/l at pH 3.1 gave no measurable color reduction, but, as in the case of dyeing wastewater no. 11, when the PAC was coupled with coagulation, the resulting treatment was very effective. Eight mg/l of alum, as Al, was applied to the waste at pH 5 and, following mixing and settling, the supernatant was withdrawn and treated by various doses of Nuchar D-14. Fig-

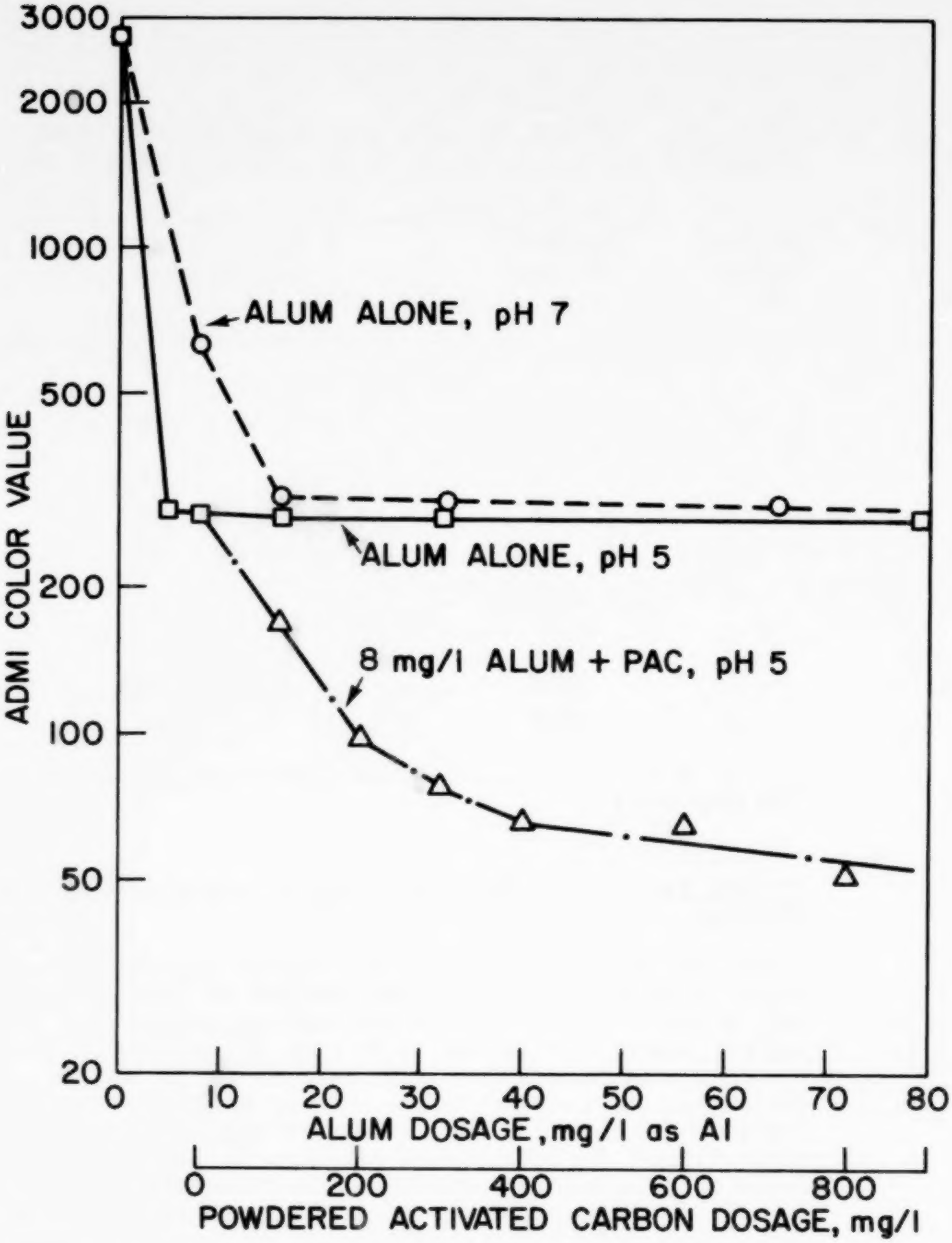

FIGURE 56. Dyeing Wastewater No. 12 (Direct Developed Dye on Rayon): Color Removal by Alum Coagulation Alone and by Two-Stage Sequence Involving Alum Coagulation and Powdered Activated Carbon Adsorption

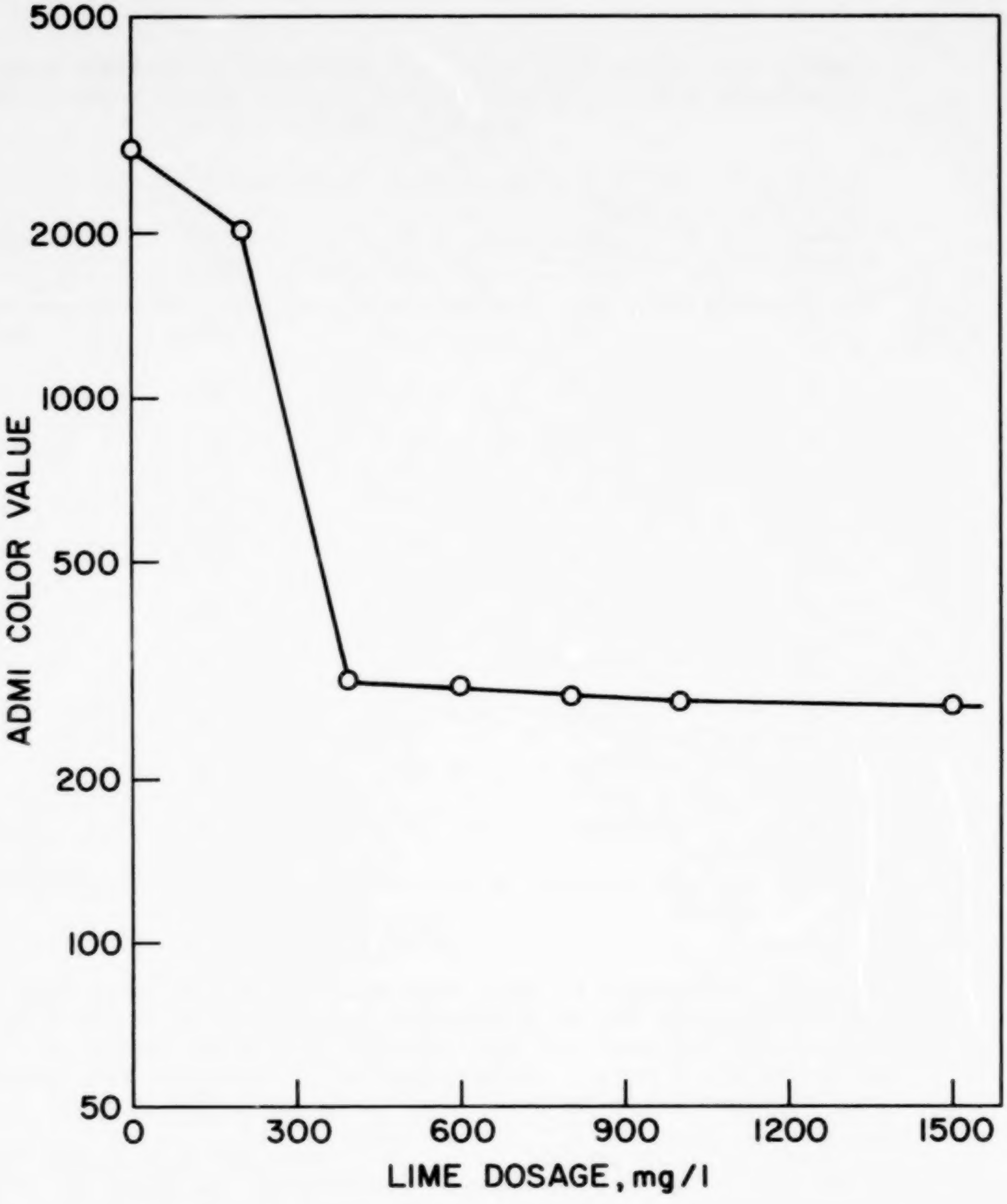

FIGURE 57. Dyeing Wastewater No. 12 (Direct Developed Dye on Rayon): Decolorization by Lime

TABLE 57. EFFECT OF ALUM AND POWDERED ACTIVATED CARBON ON TREATMENT OF DYEING WASTEWATER NO. 12 (DIRECT DEVELOPED DYE ON RAYON)

Al(III) dosage, mg/l	PAC[a] dosage, mg/l	pH	TOC, mg/l	ADMI color
0	0	3.2	56	2730
5	0	5.0	29	290
8	0	5.0	23	282
16	0	5.0	19	279
8	0	5.1	20	284
8	100	5.1	17	169
8	200	5.1	6	98
8	300	5.1	2	78
8	400	5.1	3	66
0	1000	3.1	29	2389

[a] NUCHAR D-14

ure 56 and Table 57 show the results of the combined treatment; the two stage treatment consisting of 8 mg/l of aluminum and 200 mg/l of PAC reduced the color below 100 and the TOC to 6 mg/l. Additional color removal was observed at higher carbon doses. The final BOD_5 was 1 mg/l.

Ozonation also proved to be an effective method of treating the direct developed dyeing wastewater as shown in Figures 58 and 59. Figure 58 shows that pH has very little effect on the treatment of the waste; the rates of decolorization appear to be parallel, the only difference being that the sample at pH 3.5 had a higher initial color than the sample at pH 6.7. The two runs were made on different days and apparently there was some change in the color of the sample during storage. Figure 59 shows that the partial pressure

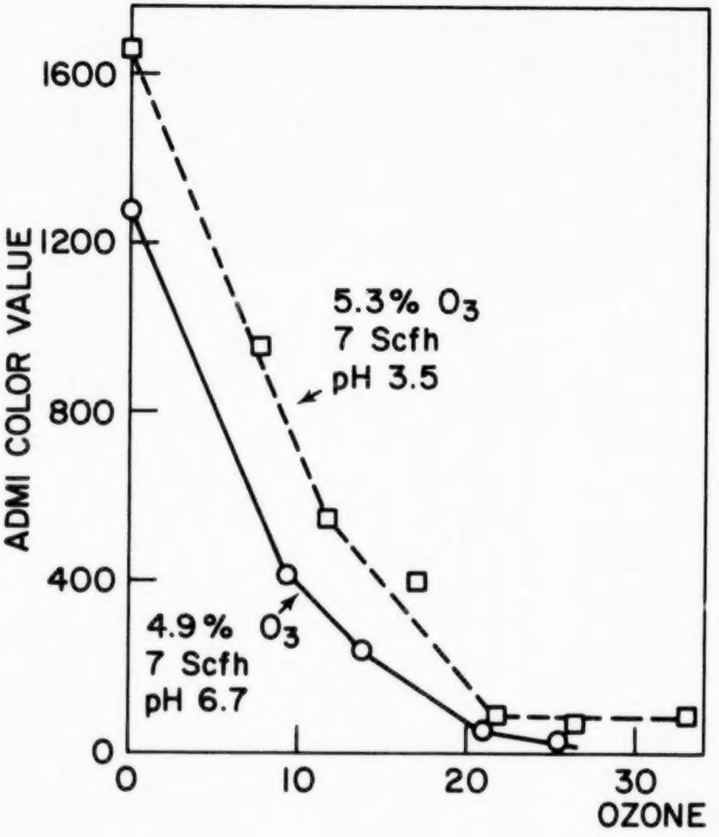

FIGURE 58. Dyeing Wastewater No. 12 (Direct Developed Dye on Rayon): Effect of pH on Decolorization by Ozone

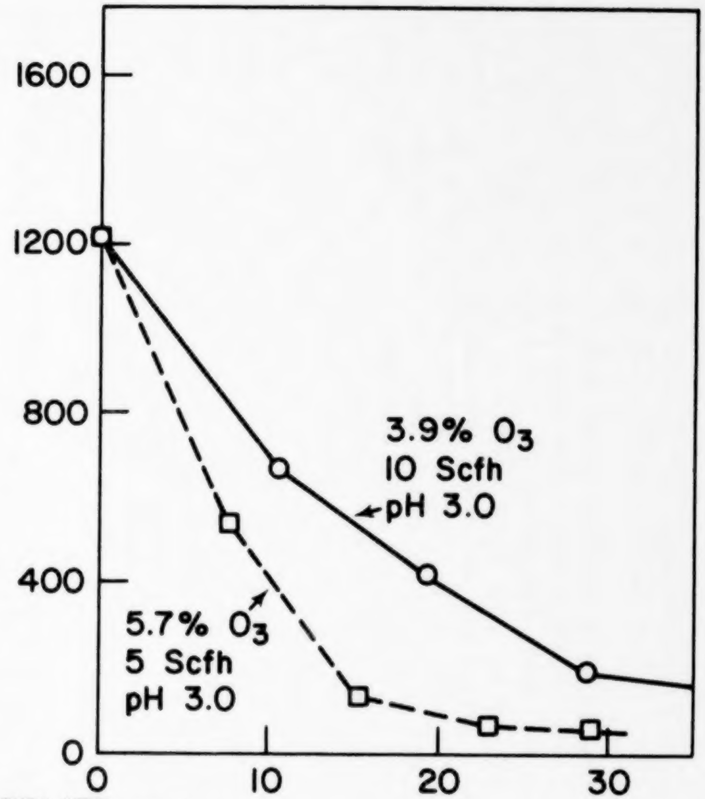

FIGURE 59. Dyeing Wastewater No. 12 (Direct Developed Dye on Rayon): Effect of Ozone Partial Pressure on Decolorization

of ozone significantly affected the degree of decolorization. The amount of ozone produced by the generator is dependent upon the rate of gas flow through the unit, so that at lower gas flow rates, a gas stream with a greater partial pressure of ozone is produced by the generator. Figure 59 shows that the ozone was more effectively utilized in decolorizing the waste when it was present at a greater volumetric percentage of the gas flow. With about 5% ozone by volume, the waste was decolorized to less than 100 by the application of 21 gms of ozone (approximately 3.5 mg/l). A very small reduction in TOC was measured and the BOD increased slightly for all samples. (It should be noted that the color of the waste immediately prior to treatment by ozonation was appreciably less than the initial color of the fresh waste (2730 ADMI color units) pointing to instability of the waste during storage. The ozone runs were made following several weeks of storage.) Figure 85e shows the appearance of one of the samples following ozonation.

Dyeing Wastewater No. 13. Disperse, Acid and Basic Dyes on Polyamide Carpet - Exhaust

Coagulation of this combination wastewater with alum, at doses up to 160 mg/l as Al at pH 7, gave little reduction in apparent color and only a small removal of TOC. Application of lime at doses up to 4000 mg/l (pH 12.2) resulted in very little change in color.

Activated carbon adsorption proved to be an effective method for treating the combined disperse/acid/basic dyeing wastewater as illustrated in Figure 60. Five different types of powdered carbon were investigated as shown in Table 58, with Darco KB proving to be the most effective. The Darco KB was tested at a dosage of 800 mg/l at 5 different pH values as shown in Table 59, and pH 3 is seen to be the most effective in both color and TOC removal. Figure 60 shows the effect of various dosages of the Darco KB on the apparent ADMI color at two different pH values. It is apparent that a carbon dosage of 500 mg/l at pH 3 was sufficient to reduce the apparent color to 40. Similarly, Figure 61 indicates that TOC removal by Darco KB was more effective at pH 3, with 500 mg/l reducing the TOC concentration to 50 mg/l and 1000 mg/l reducing the TOC to 22 mg/l. Figures 85f and 85g show the apparent color of the treated samples for the different types of PAC and for Darco KB at pH 3.

Ozonation also proved to be an effective means of decolorizing the combination dyeing wastewater. Figure 62 shows

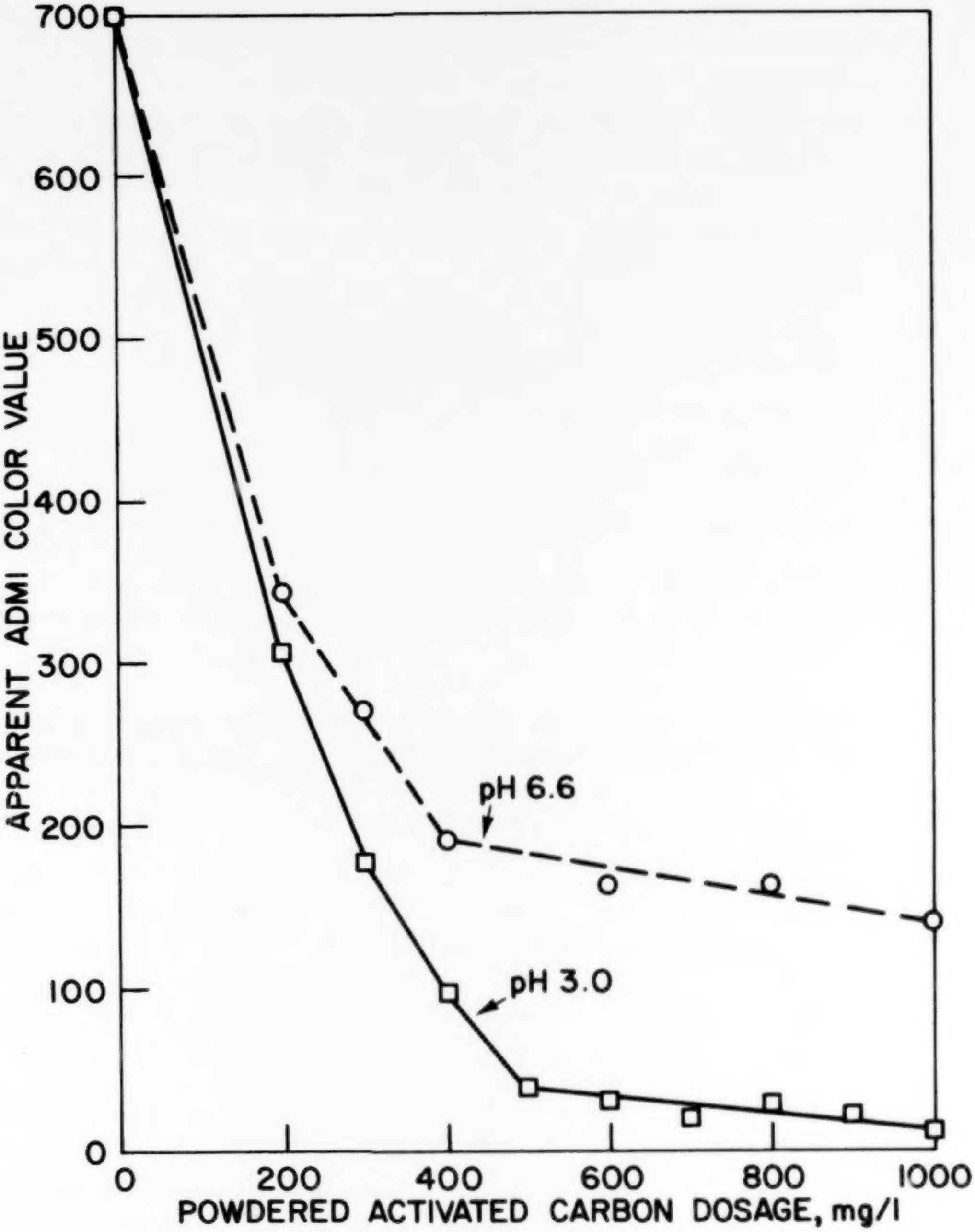

FIGURE 60. Dyeing Wastewater No, 13 (Disperse, Acid and Basic Dyes on Polyamide Carpet): Color Removal by Powdered Activated Carbon Adsorption

TABLE 58. EFFECT OF DIFFERENT TYPES OF POWDERED ACTIVATED CARBONS ON TREATMENT OF DYEING WASTEWATER NO. 13 (DISPERSE/ ACID/BASIC DYES ON POLYAMIDE CARPET)

Type of PAC	Dosage, mg/l	pH	TOC, mg/l	Apparent color
NUCHAR D-14	800	6.5	56	307
NUCHAR D-16	800	6.5	53	310
DARCO KB	800	6.6	42	233
DARCO HDB	800	6.7	66	370
DARCO HD-3000	800	6.6	60	301

TABLE 59. EFFECT OF pH ON TREATMENT OF DYEING WASTEWATER NO. 13 (DISPERSE/ACID/BASIC DYES ON POLYAMIDE CARPET) BY POWDERED ACTIVATED CARBON

Dosage of DARCO KB, mg/l	pH	TOC, mg/l	Apparent color
800	6.6	50	193
800	6.0	47	236
800	5.0	43	207
800	4.0	39	139
800	3.0	25	53

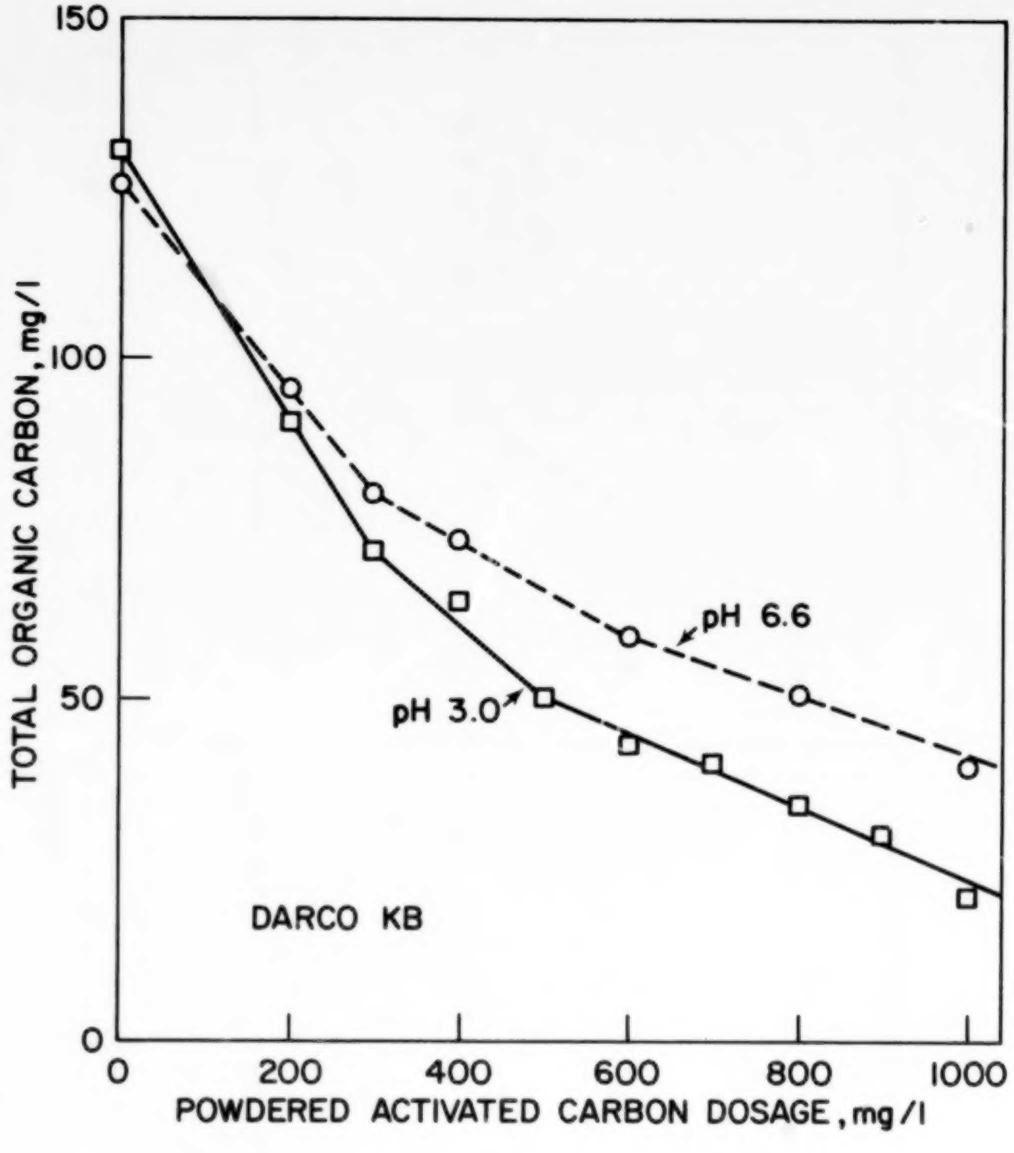

FIGURE 61. Dyeing Wastewater No. 13 (Disperse, Acid and Basic Dyes on Polyamide Carpet): Removal of Total Organic Carbon by Powdered Activated Carbon

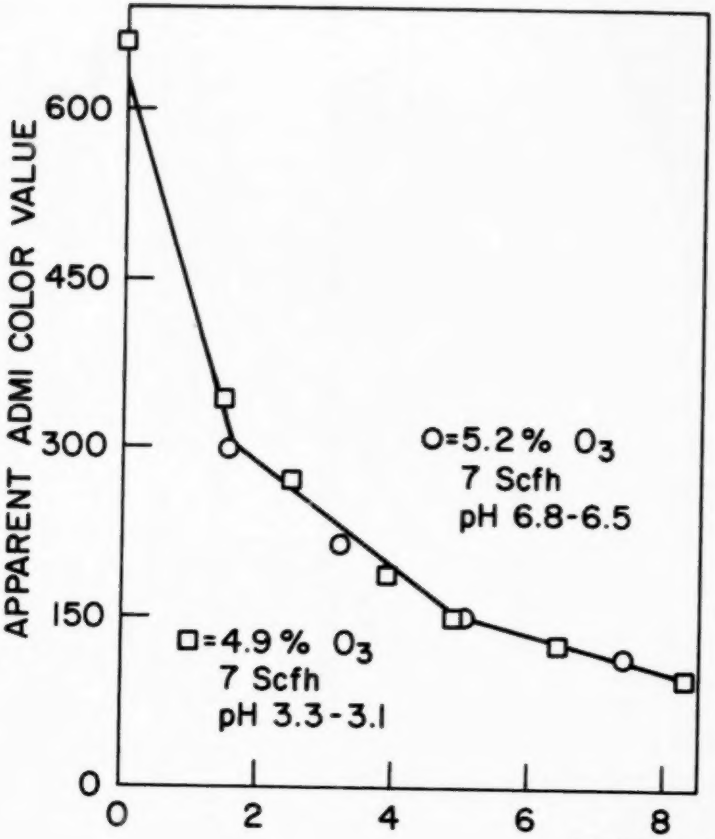

FIGURE 62. Dyeing Wastewater No. 13 (Disperse, Acid and Basic Dyes on Polyamide Carpet): Effect of pH on Decolorization by Ozone

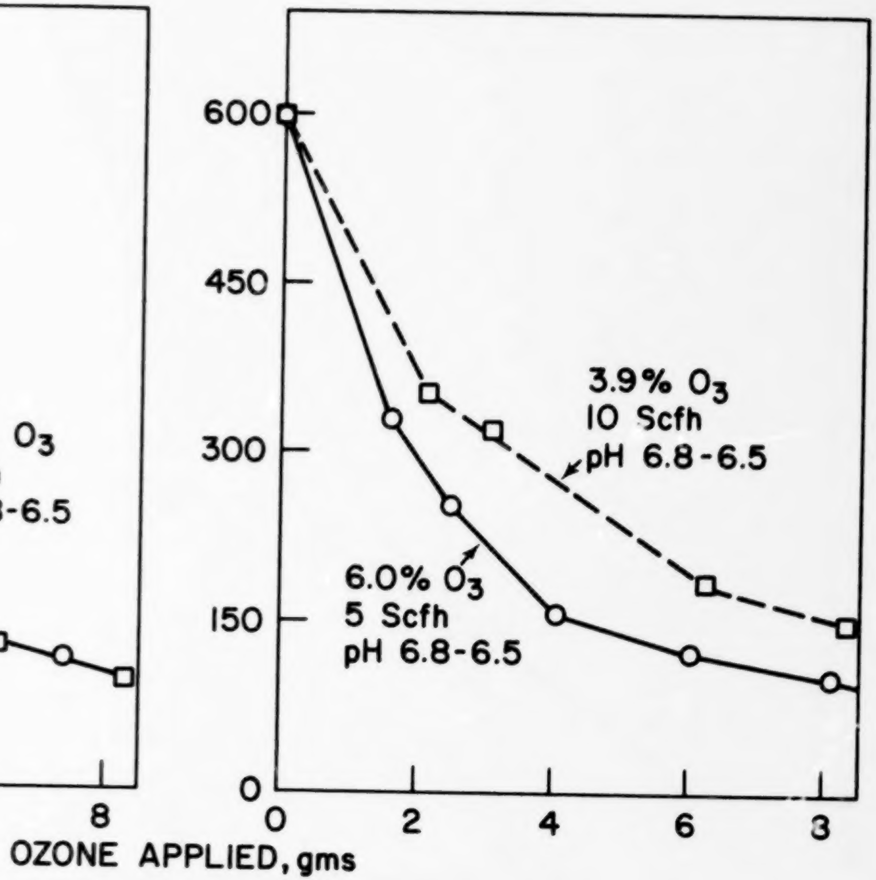

FIGURE 63. Dyeing Wastewater No. 13 (Disperse, Acid and Basic Dyes on Polyamide Carpet): Effect of Ozone Partial Pressure on Decolorization

that decolorization was not affected by pH with similar degrees of decolorization achieved at pH 3.3 and pH 6.8. Figure 63 shows the effect of the ozone partial pressure on the efficiency of decolorization; increased partial pressures of ozone, again generated by lower gas flow rates through the generator, provided for more effective utilization of ozone in decolorizing the waste. At a 5% ozone concentration by volume, 8 gms of ozone (1.3 gm/l) was sufficient to decolorize the waste to an apparent ADMI color of 100. There was no reduction in total organic carbon but in all four samples tested, BOD increased as a result of ozonation.

In order to determine how efficiently ozone was utilized by the wastewater in the given reactor configuration, the ozonation run at neutral pH was repeated and the off-gas collected and analyzed for its residual ozone concentration. The off-gas was passed through a series of neutral buffered KI absorbing solutions, over several different time periods and the resulting I_2 was titrated with standardized thiosulfate. The data for the run are presented in Table 60 and the key features are illustrated in Figure 64. The total absorption of ozone by the system over the 17-min run was 67.1%. It is significant that, despite the small degree of decolorization near the end of the run, a significant amount of ozone (about 60% of that applied) was still being absorbed by the waste. Although there was no removal of TOC, even near the end of the run, it is possible that some of the organic carbon was oxidized to a higher oxidation state, but not to CO_2. It is also plausible to expect that a significant portion of the apparent ozone absorbed simply decomposed to oxygen.

Dyeing Wastewater No. 14. Disperse Dye on Polyester - High Temperature Exhaust

Lime dosages of up to 1000 mg/l resulted in no apparent loss in color and no measurable reduction in TOC. Figure 65 shows decolorization of the disperse dyeing wastewater by coagulation with alum at two different pH values; pH 5 was again more effective than pH 7, but the color could not be reduced to less than 200 by alum alone. Activated carbon, at dosages of up to 1000 mg/l of Nuchar D-14 at pH 3, proved to be relatively inefficient in removing color or TOC as shown in Figure 66. Adsorption at pH 3 was more effective than at pH 10.5. A two-stage treatment was attempted combining coagulation by 65 mg/l of aluminum at pH 5 with treatment of the supernatant by Nuchar D-14, also

TABLE 60. EFFICIENCY OF OZONE ABSORPTION DURING DECOLORIZATION OF DYEING WASTEWATER NO. 13

Time, min.	ADMI color value	Ozone applied over given time interval, gms.	Cumulative ozone applied, gms.	Ozone collected in exhaust trap over given time interval, gms	Cumulative ozone in exhaust, gms.	Ozone absorbed over given time interval, gms.	Cumulative ozone absorbed, gms.	Ozone absorbed over given time interval, %
0	666	0	----	0	----	-	----	----
3	347	1.47	1.47	0.18	0.18	1.29	1.29	87.7
5	276	0.98	2.45	0.35	0.53	0.63	1.92	64.3
8	190	1.47	3.92	0.39	0.92	1.08	3.00	73.5
10	150	0.98	4.90	0.40	1.32	0.58	3.58	59.2
13	131	1.47	6.37	0.60	1.92	0.87	4.45	59.2
17	100	1.96	8.33	0.82	2.74	1.14	5.59	58.2
							Average	67.1%

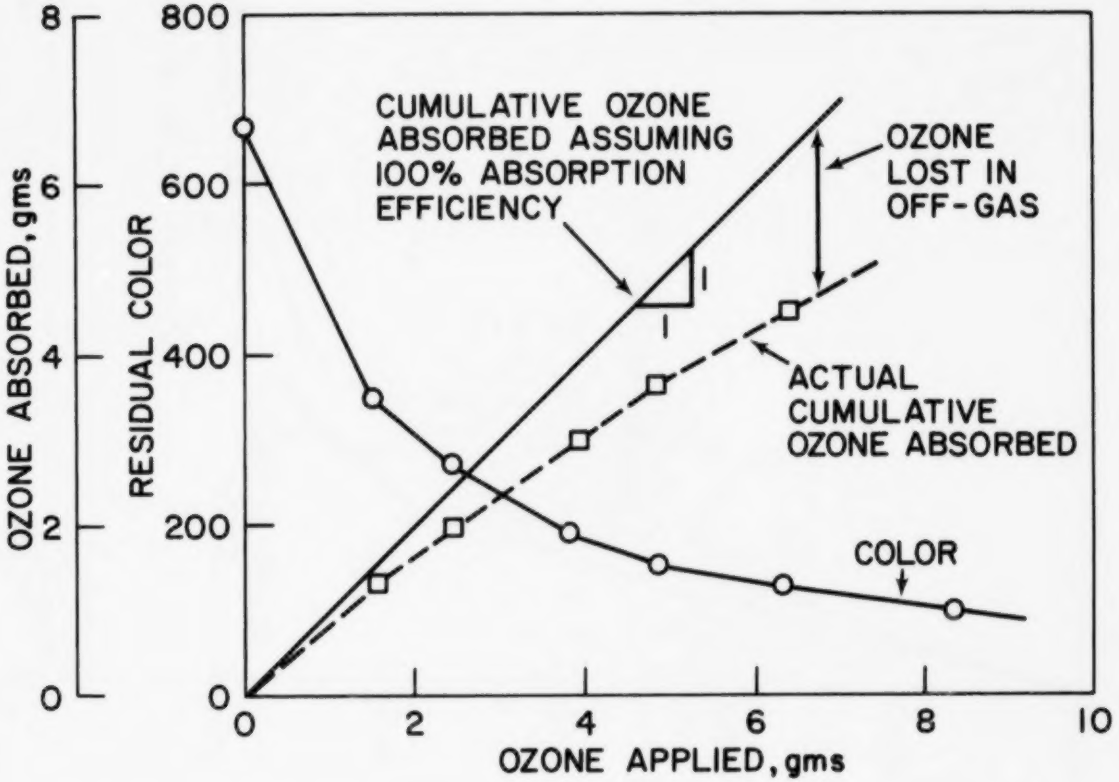

FIGURE 64. Dyeing Wastewater No. 13 (Disperse, Acid and Basic Dyes on Polyamide Carpet): Efficiency of Ozone Adsorption and Utilization

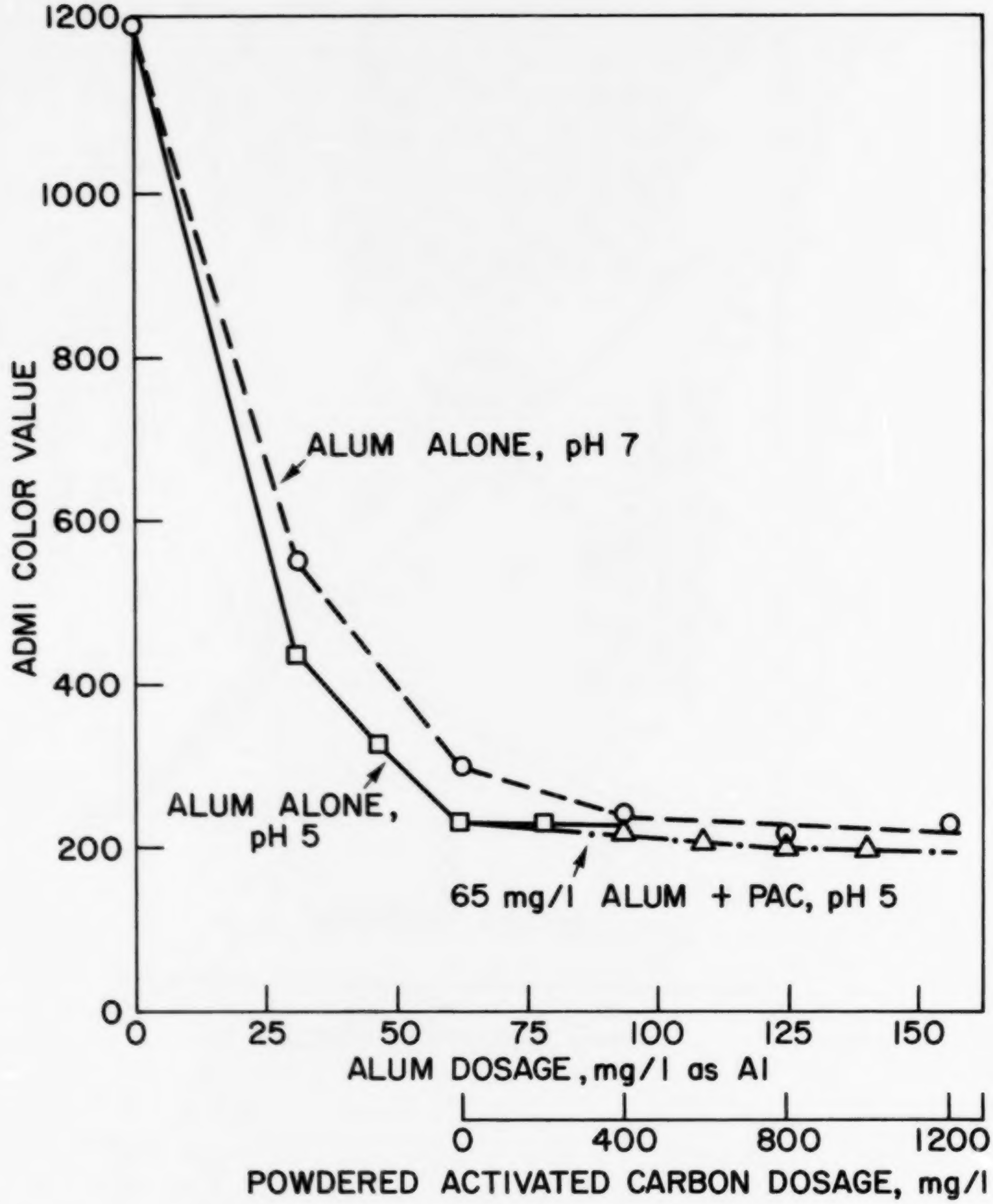

FIGURE 65. Dyeing Wastewater No. 14 (Disperse Dye on Polyester): Decolorization by Alum Coagulation Alone and by Two-Stage Sequence Involving Alum Coagulation and Powdered Activated Carbon Adsorption

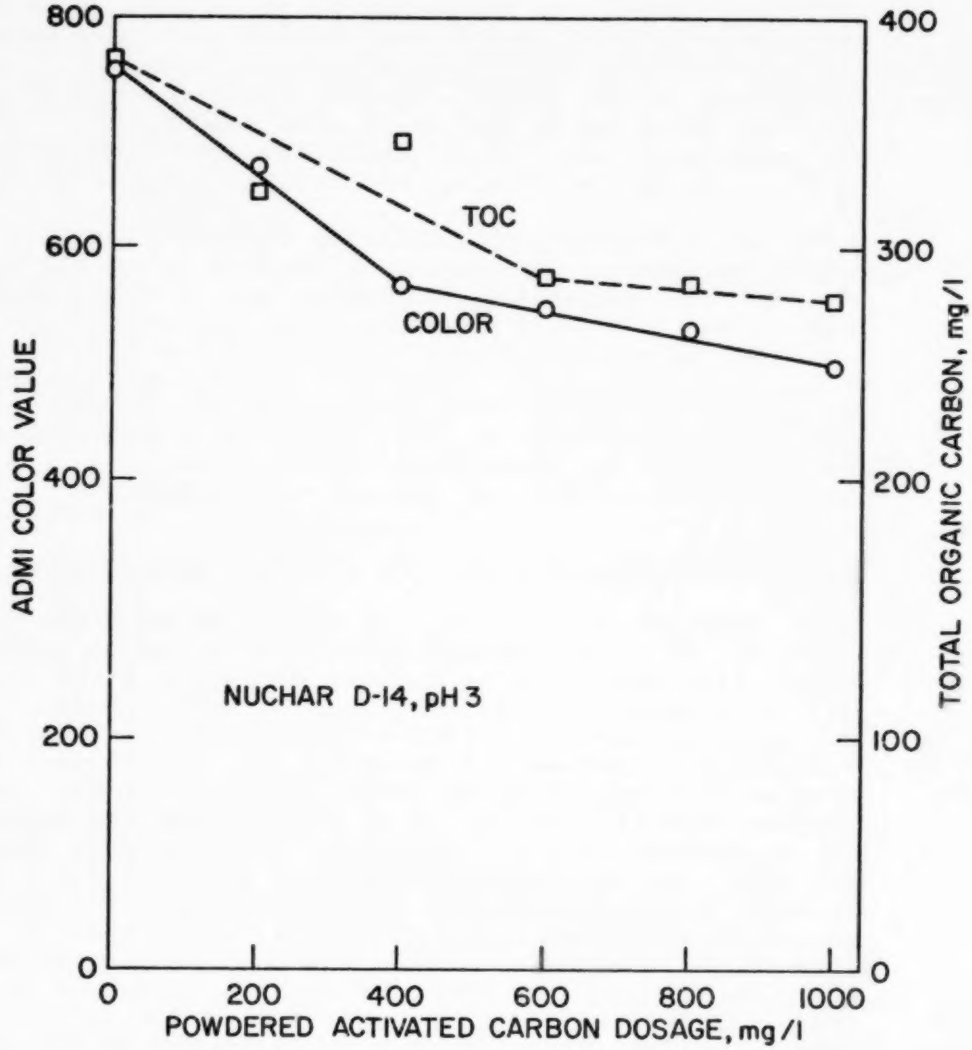

FIGURE 66. Dyeing Wastewater No. 14 (Disperse Dye on Polyester): Color and Total Organic Carbon Removal by Powdered Activated Carbon Alone

at pH 5. Figure 65 shows that the powdered carbon had no additional effect on the color of the waste. Five different types of activated carbon were tested, but none were effective in reducing the color further. The nature of the residual color is not known. TOC was reduced approximately 65% by alum, as shown in Figure 67, and removal was enhanced by the subsequent addition of PAC. BOD_5 was reduced by 50%, to 96 mg/l, by coagulation with alum alone, at pH 5.

Ozone was moderately effective in decolorizing the disperse dyeing wastewater as shown in Figure 68. The wastewater contained an appreciable concentration of surfactant as foaming was excessive when the O_3/O_2 gas stream was diffused into the column; a defoaming agent was required in order to control the foam. The waste was readily decolorized by 20 gms of ozone (approximately 3.5 gms/l) to 400, but continued ozonation did not decolorize the waste further. Figure 85h shows the appearance of the ozonated samples. The concentration of TOC was reduced only slightly.

Dyeing Wastewater No. 15. Sulfur Dye on Cotton - Continuous

Lime, alum and ferric iron all proved to be effective coagulants of the sulfur dyeing wastewater as shown in Figure 69. Again, alum was found to be more effective at pH 5 than at pH 7 with doses of only 8 mg/l as Al sufficient to reduce the color to less than 100; 17 mg/l of Fe(III) at pH 7 was sufficient to reduce the color to 105, but Fe(III) should be even more efficient at lower pH values (5-6). Five hundred mg/l of lime (pH 11.0) decolorized the sulfur dyeing wastewater to 100. It should be noted that the resultant floc from the additions of lime and alum did not settle as well as the floc formed by ferric iron. The waste sample was extremely foamy and a scum layer was formed on the surface of all treated samples. Powdered carbon, at dosages of up to 1000 mg/l of Darco KB at pH 3.8, showed no apparent color reduction. Despite the effective decolorization by lime, alum and iron, little removal of TOC or BOD was achieved. (A large part of the residual oxygen demand was probably due to the presence of sulfides and polysulfides.) Figure 85i shows the appearance of the samples after coagulation by lime and alum.

Ozone was also relatively effective in decolorizing the sulfur dyeing wastewater but, again, due to the extremely high surfactant content of the waste, a defoaming agent had to be added. Figure 70 shows the effect of various dosages of ozone on residual ADMI color at the initial pH of the raw

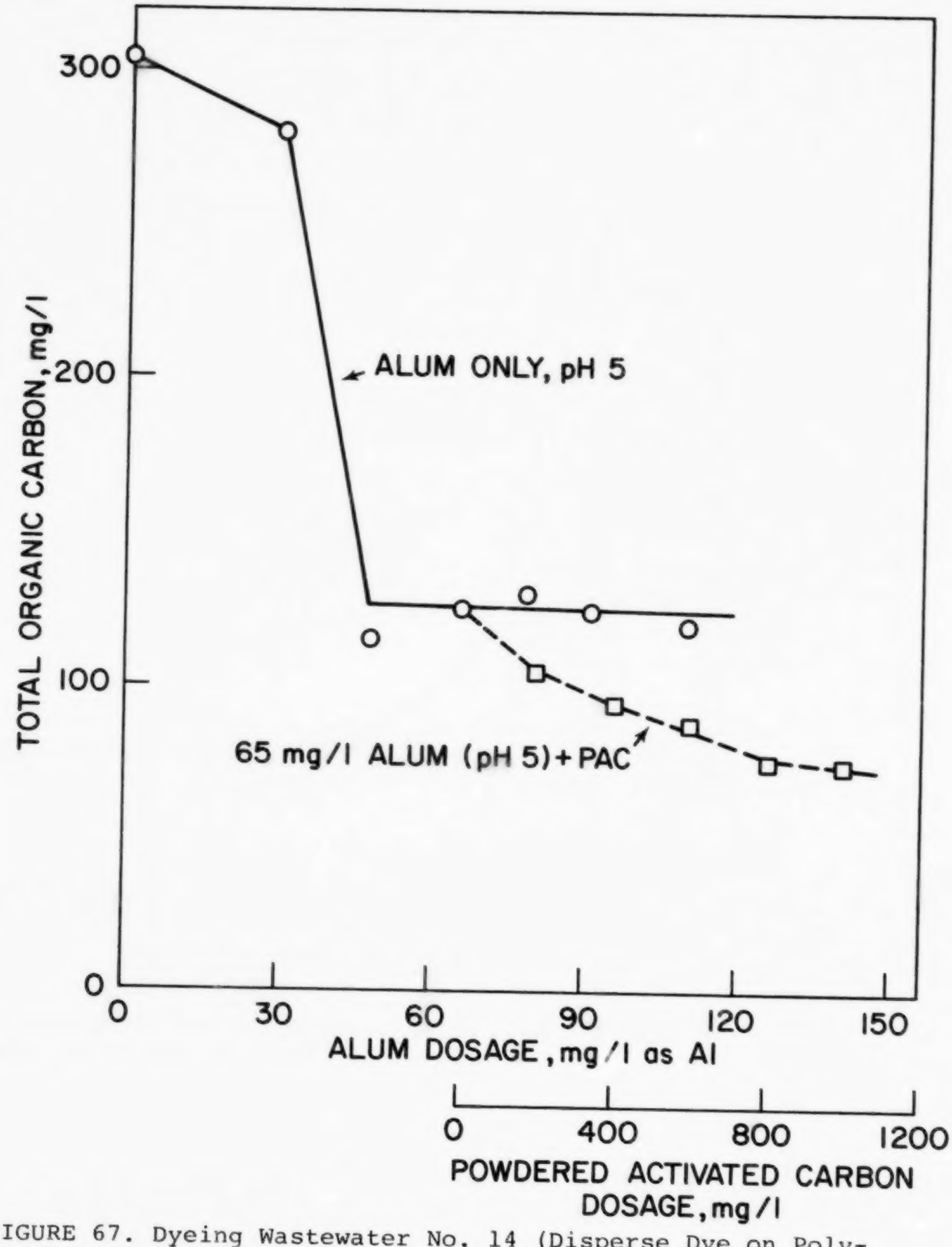

FIGURE 67. Dyeing Wastewater No. 14 (Disperse Dye on Polyester): Removal of Total Organic Carbon by Alum Coagulation Alone and by Two-Stage Sequence Involving Alum Coagulation and Powdered Activated Carbon Adsorption

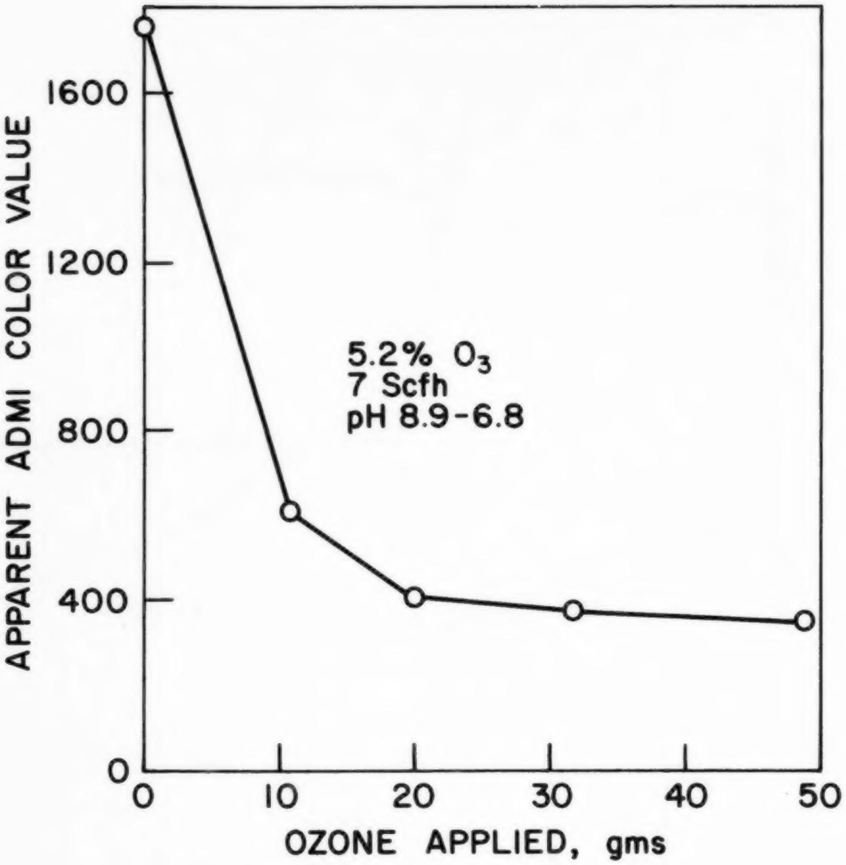

FIGURE 68. Dyeing Wastewater No. 14 (Disperse Dye on Polyester): Decolorization by Ozone

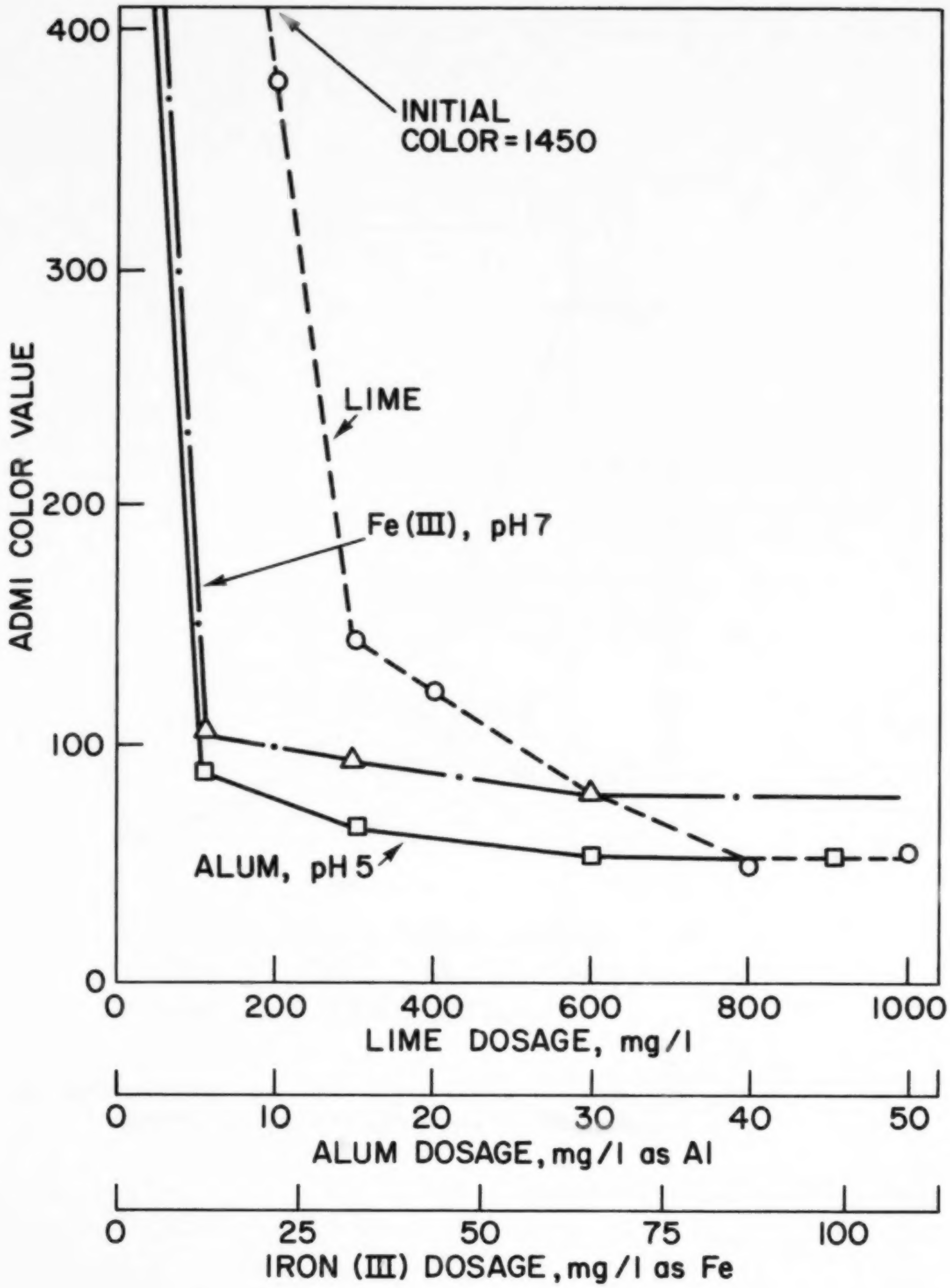

FIGURE 69. Dyeing Wastewater No. 15 (Sulfur Dye on Cotton): Color Removal by Lime, Alum, and Iron(III) Coagulation

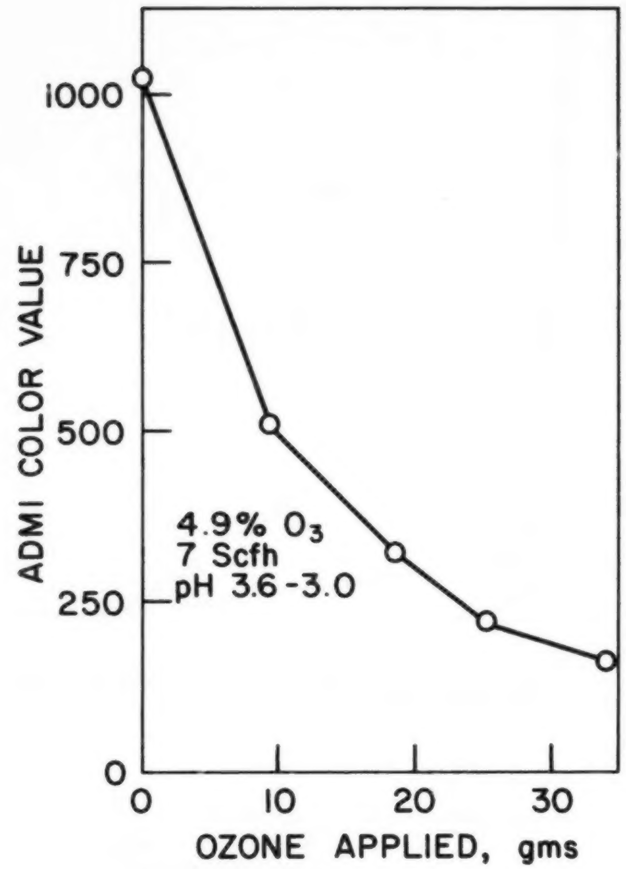

FIGURE 70. Dyeing Wastewater No. 15 (Sulfur Dye on Cotton): Decolorization by Ozone

waste. pH decreased slightly during the course of ozonation, and 35 gms of ozone (approximately 6 gm/l) was required to decolorize the sample to a value of 150. A parallel run was also conducted at pH 5.8 and the data points coincide with the plot in Figure 70, suggesting that, in the acidic pH range, there is no effect of pH on decolorization by ozone. No reduction in TOC or BOD was found.

Dyeing Wastewater No. 16. Reactive Dye on Cotton - Continuous

Dosages of aluminum up to 160 mg/l at pH 7 resulted in no apparent reduction in color and only a 30% reduction in TOC. Lime was also ineffective in removing color or TOC at doses up to 1000 mg/l. In contrast, Figure 71 and Tables 61 and 62 show the effect of powdered carbon on the color of the reactive dyeing wastewater. Six types of powdered carbon were tested, with Darco HDB and KB being most effective (see Table 61); decolorization was best at pH 6 (see Table 62). Figure 71 shows that a dosage of 1600 mg/l of Darco HDB at pH 6.0 was required to reduce the color of the reactive dye to 100. TOC was also removed by PAC more effectively at pH 6 than at pH 9, but the degree of removal was only about 30% (see Figure 72). Figure 85j shows the appearance of the samples after adsorption by Darco HDB at pH 6.

Ozone was very effective in decolorizing the reactive dyeing wastewater as shown in Figure 73; decolorization was more effective at the acidic pH value (pH 3.9) than at the slightly alkaline pH value of the raw waste (pH 8.5) despite the slightly lower partial pressure of ozone in the run at pH 3.9. Under the acid conditions, the color was reduced to less than 100 by the application of 7.5 gms of ozone (1.25 gm/l). TOC and BOD were unchanged.

Dyeing Wastewater No. 17. Vat and Disperse Dyes on Polyester/Cotton - Continuous

Coagulation of the combination vat and disperse dyeing wastewater by alum proved to be an effective means of treatment as shown in Figure 74. Runs were made holding pH constant at 7 and 5 by the concurrent addition of acid or base along with the alum. Decolorization, as before, was more effective at the lower pH. A third run with alum was made with no concurrent pH adjustment and the residual color of these samples are shown by the solid line in Figure 74, with the pH values indicated in parentheses. The sample at 50 mg/l of aluminum had a final pH of 6.0 and effected the same

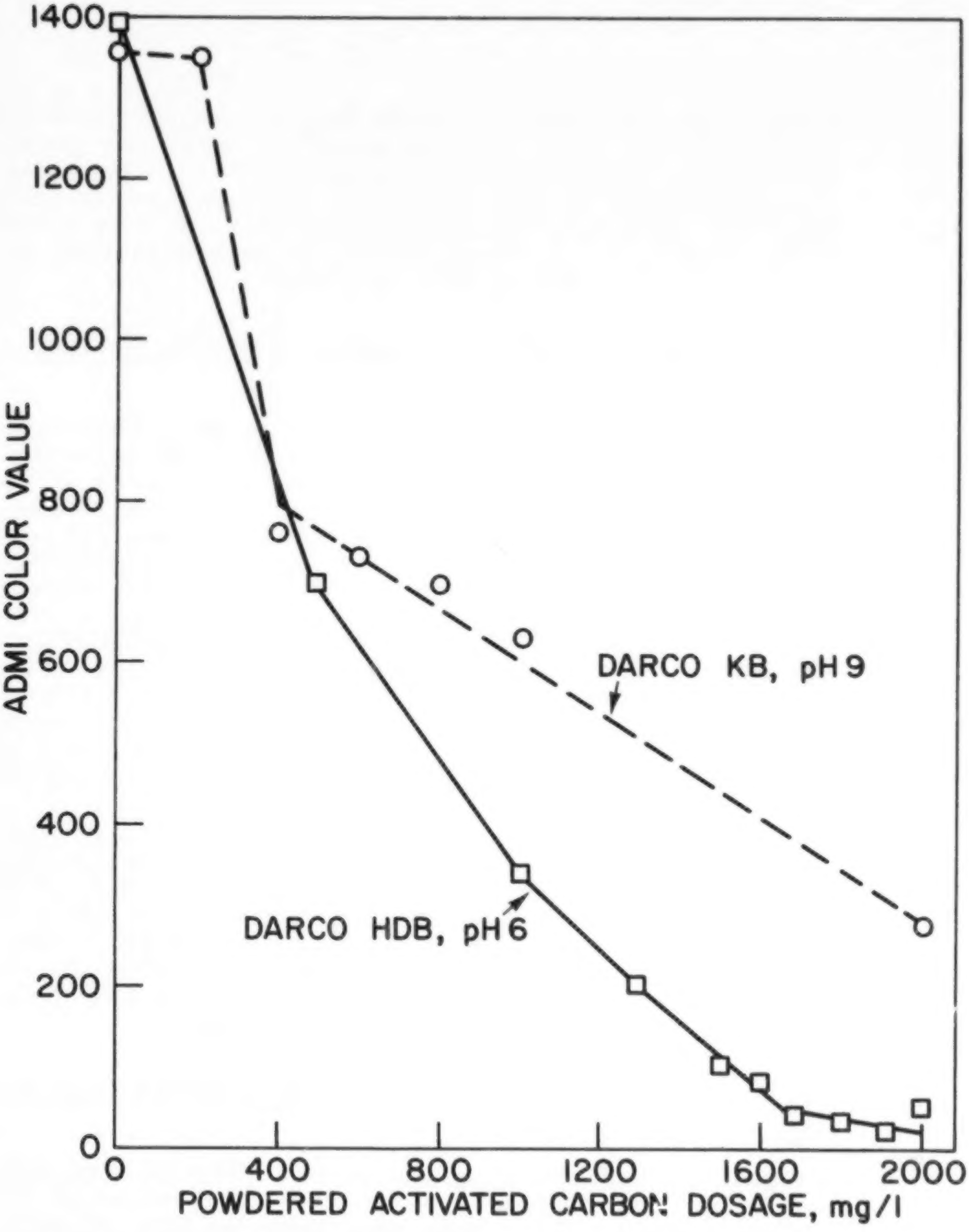

FIGURE 71. Dyeing Wastewater No. 16 (Reactive Dye on Cotton): Decolorization by Powdered Activated Carbon

TABLE 61. EFFECT OF DIFFERENT TYPES OF POWDERED ACTIVATED CARBONS ON TREATMENT OF DYEING WASTEWATER NO. 16 (REACTIVE DYE ON COTTON)

Type of PAC	Dosage, mg/l	pH	TOC, mg/l	ADMI color
NUCHAR D-14	1000	8.6	180	757
NUCHAR D-16	1000	8.4	188	708
DARCO HDB	1000	9.1	177	580
DARCO HD-3000	1000	9.1	183	710
DARCO KB	1000	8.9	168	628
HYDRODARCO C	1000	9.0	187	754

TABLE 62. EFFECT OF pH ON TREATMENT OF DYEING WASTEWATER NO. 16 (REACTIVE DYE ON COTTON) BY POWDERED ACTIVATED CARBON

Dosage of DARCO HDB, mg/l	pH	TOC, mg/l	ADMI color
1000	9.1	167	609
1000	8.0	166	481
1000	7.0	151	418
1000	6.0	159	257
1000	5.0	158	305
1000	4.0	160	300

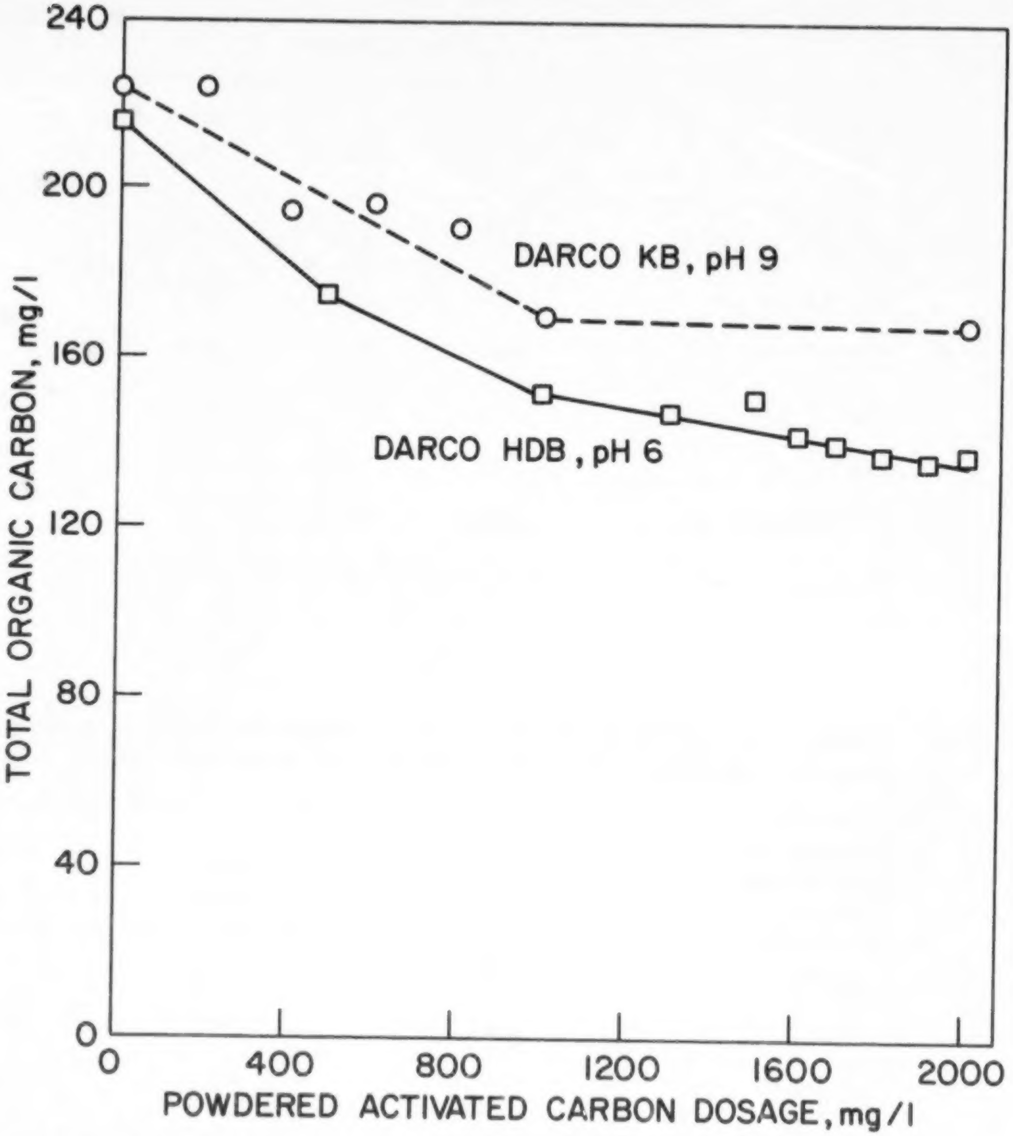

FIGURE 72. Dyeing Wastewater No. 16 (Reactive Dye on Cotton): Removal of Total Organic Carbon by Powdered Activated Carbon

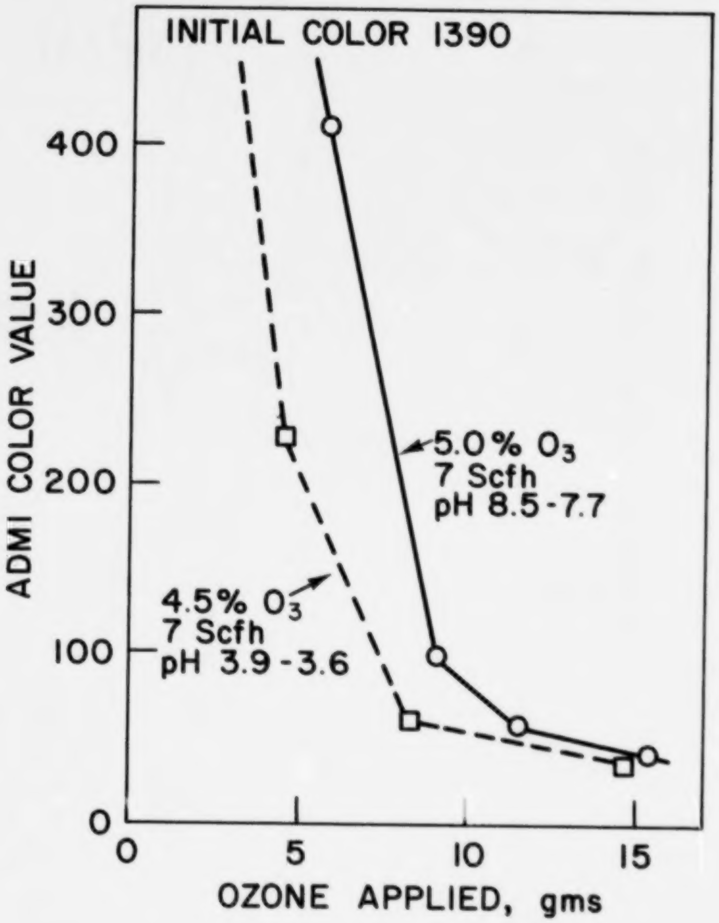

FIGURE 73. Dyeing Wastewater No. 16 (Reactive Dye on Cotton): Decolorization by Ozone

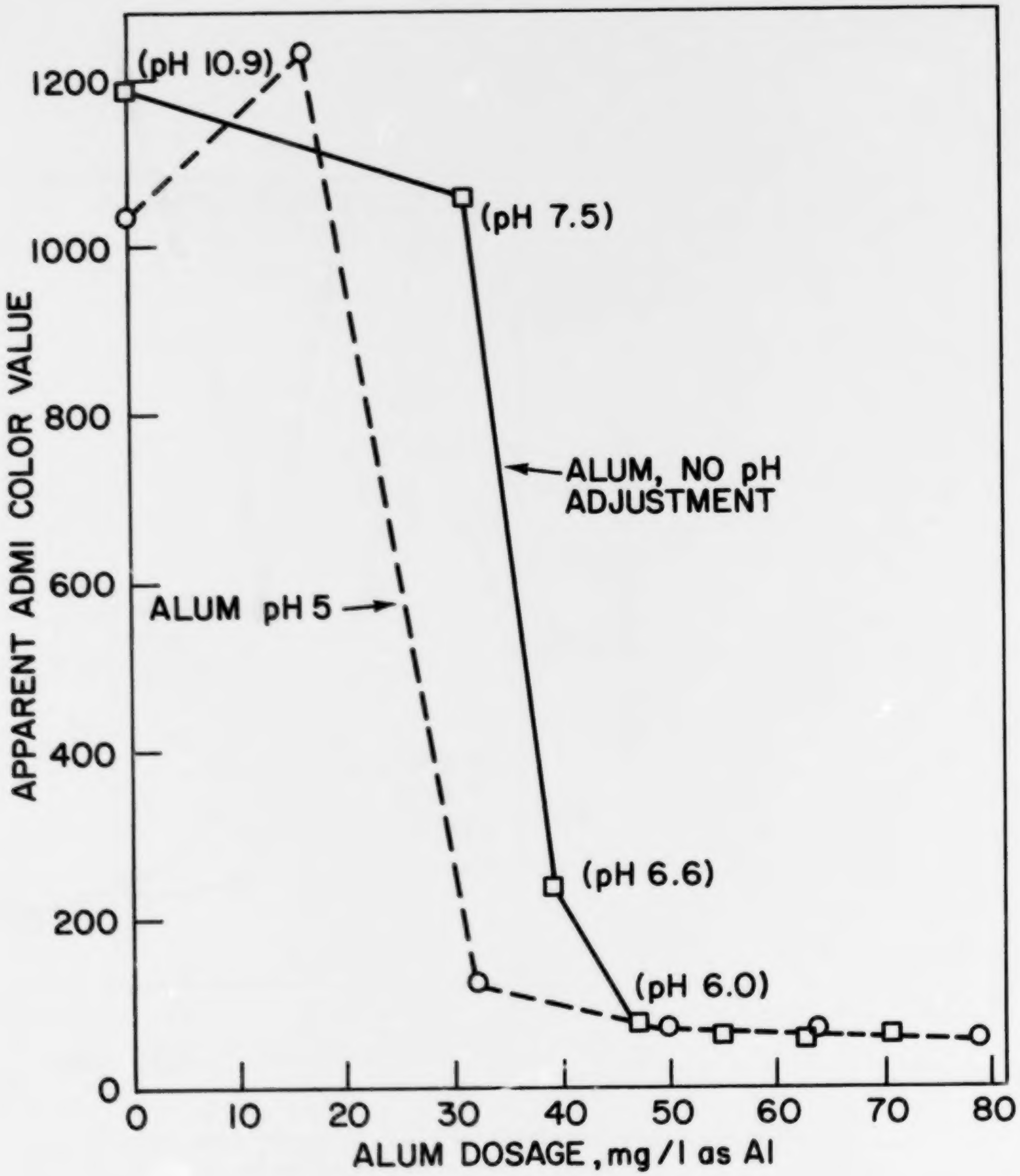

FIGURE 74. Dyeing Wastewater No. 17 (Disperse and Vat Dyes on Polyester/Cotton): Color Removal by Alum Coagulation

degree of decolorization as the sample treated with alum and adjusted to pH 5. Hence, due to the high initial alkalinity of this particular waste, the addition of 50 mg/l of alum (an acid) brought the pH of the waste into the proper range for effective coagulation. The final apparent color value at 50 mg/l of Al(III) was 80, as shown. TOC removal was about 25%. Figure 85k shows the appearance of the samples following coagulation by alum. (It should be mentioned that although good removal of color was achieved, the supernatant still foamed appreciably.)

Lime, at doses up to 1000 mg/l, produced no noticeable floc and gave no apparent reduction in color. Powdered activated carbon (Darco KB) was somewhat effective in decolorizing the waste as shown in Figure 75, with color removal at pH 3.3 better than that at pH 11.0 but not as efficient as that achieved by alum. The degree of TOC removal was small, as shown.

Ozonation proved to be a relatively inefficient means of decolorizing the combined vat/disperse dyeing wastewater. Figure 76 shows that the apparent color could only be reduced to 400 by the application of 50 gms of ozone (approximately 8.5 gm/l) at the alkaline pH value indicated; pH decreased during the course of ozonation. A parallel run under acidic conditions (pH 4.5 dropping to pH 3.2) resulted in a reduction in color to only 870 by the application of 15 gm of ozone. TOC was reduced only slightly in both runs. (A defoaming agent had to be added to control the foam.)

Dyeing Wastewater No. 18. Basic Dyes on Polyester - Exhaust

Alum was ineffective in coagulating the basic dyeing wastewater; although good floc were formed, no apparent color reduction was noted at aluminum doses up to 160 mg/l at pH 5. Lime doses up to 1000 mg/l (pH 12.2) resulted in no floc formation and little reduction in color. Activated carbon, however, proved to be a very effective adsorbent of the basic dyes. Table 63 shows that Nuchars D-14 and D-16 and Darco KB were the most effective decolorizing carbons of those tested, and Table 64 shows that decolorization was best at pH 6-7. Figure 77 illustrates decolorization of the waste by various doses of Darco KB at pH 5 (the pH of the raw dyeing wastewater); 700 mg/l of the carbon reduced the color to 100, with increased carbon doses resulting in further decolorization. A parallel run with Nuchar D-16 at pH 5 gave the same degree of color removal as the Darco KB. Additional runs with both Darco KB and Nuchar D-16 at pH 7 confirmed the data in Table 64 that, for this particular

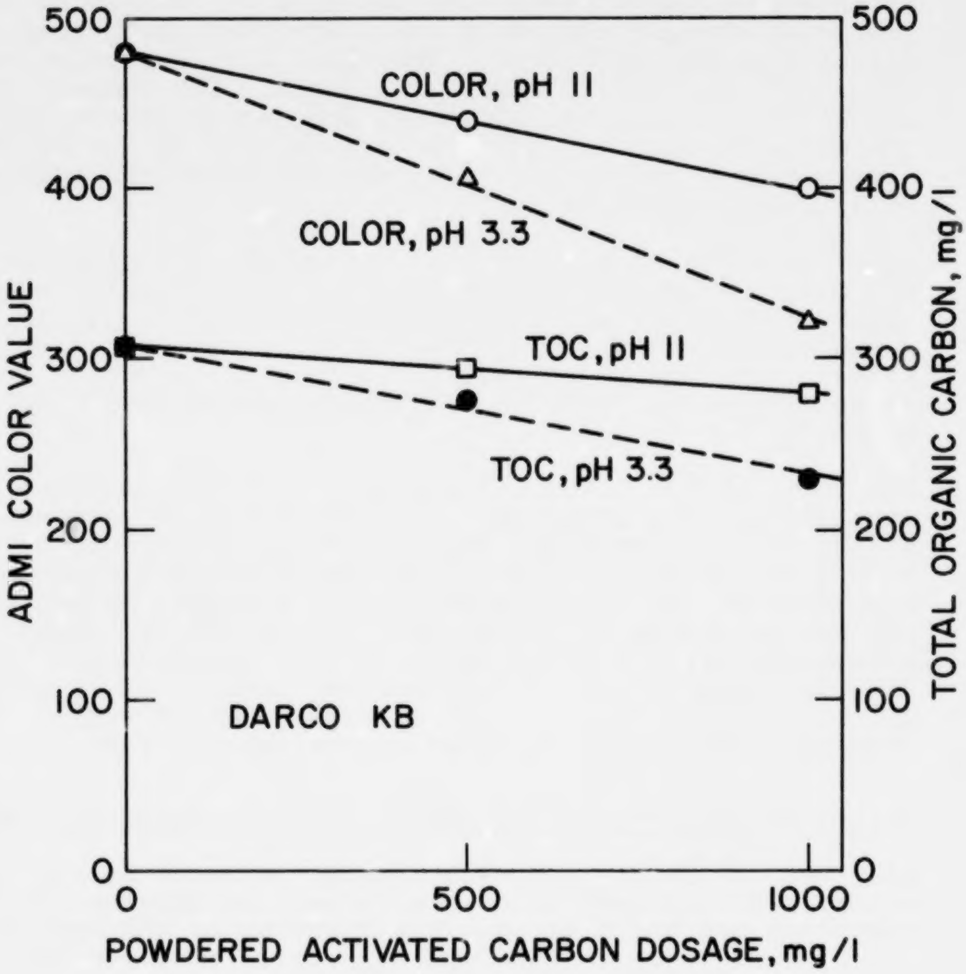

FIGURE 75. Dyeing Wastewater No. 17 (Disperse and Vat Dyes on Polyester/Cotton): Color and Total Organic Carbon Removal by Powdered Activated Carbon

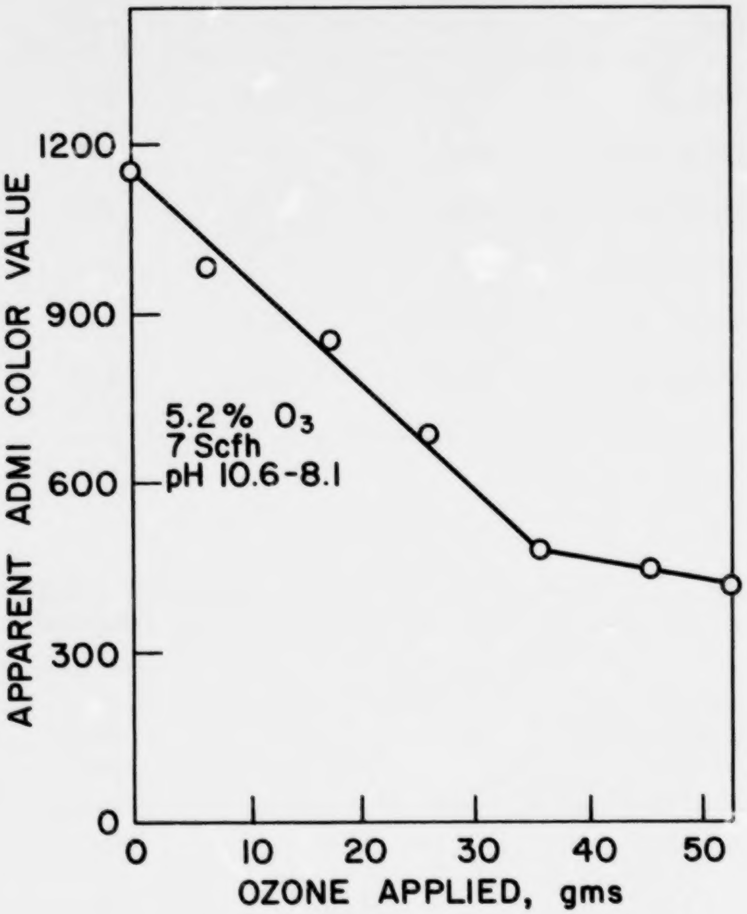

FIGURE 76. Dyeing Wastewater No. 17 (Disperse and Vat Dyes on Polyester/Cotton): Decolorization by Ozone

TABLE 63. EFFECT OF DIFFERENT TYPES OF POWDERED ACTIVATED CARBONS ON TREATMENT OF DYEING WASTEWATER NO. 18 (BASIC DYES ON POLYESTER)

Type of PAC	Dosage, mg/l	pH	TOC, mg/l	Apparent color
DARCO KB	400	5.0	700	262
DARCO HDB	400	5.3	970	1610
DARCO HD-3000	400	4.9	780	1630
HYDRODARCO C	400	5.2	860	1673
NUCHAR D-14	400	5.0	860	167
NUCHAR D-16	400	5.0	850	128

TABLE 64. EFFECT OF pH ON TREATMENT OF DYEING WASTEWATER NO. 18 (BASIC DYES ON POLYESTER) BY POWDERED ACTIVATED CARBON

Dosage of NUCHAR D-16, mg/l	pH	TOC, mg/l	Apparent color
400	3.0	750	249
400	4.0	980	172
400	5.0	910	163
400	6.0	755	110
400	7.0	815	104

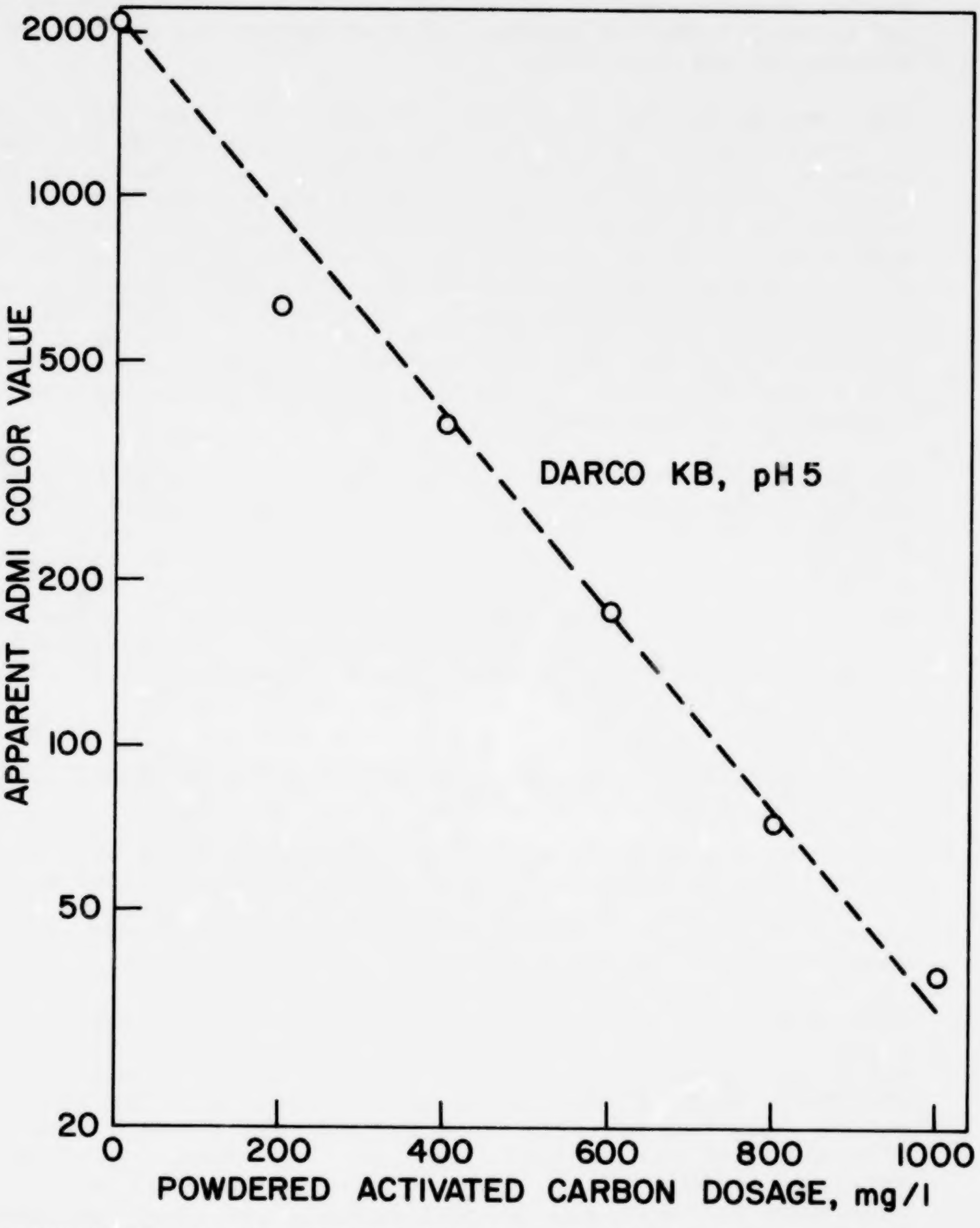

FIGURE 77. Dyeing Wastewater No. 18 (Basic Dyes on Polyester): Decolorization by Powdered Activated Carbon

waste, decolorization by carbon adsorption was more effective under conditions of neutral pH than under the acidic pH conditions of the raw waste.

TOC removal by PAC is shown in Figure 78. The initial TOC of the raw waste was quite high (this wastewater had the highest concentration of TOC and BOD of all twenty of the dyeing wastewaters generated) and although the quantity (by weight) of TOC removed by 1000 mg/l of Darco KB at pH 5 was appreciable, it only amounted to a TOC reduction of about 40%. The BOD concentration as a result of the carbon treatment, however, was unchanged. It should be noted that the treated samples still foamed upon handling. Figures 85ℓ and 85m show the effect of the different types of carbon on the waste and the effect of various doses of Nuchar D-16 on the appearance of the sample.

The basic dye was also readily decolorized by ozone but, again, control of the foam was necessary. Decolorization seemed to be more effective at lower pH values as shown in Figure 79. Despite the relatively effective decolorization to an apparent color of 300 with only 12 gms of ozone (2 gm/l), the color could not be reduced below 250. The nature of the residual color and the reason for its resistance to ozonation is unknown. There was no reduction in TOC by ozone.

Dyeing Wastewater No. 19. Disperse, Acid and Basic Dyes on Polyamide Carpet - Continuous

Figure 80 shows that only 8 mg/l of Al(III) was sufficient to decrease the color of this rather weakly-colored waste to approximately 50. The TOC concentration remained the same. No apparent color reduction was encountered, however, when lime was applied even at doses up to 1000 mg/l.

When powdered carbon was tested for decolorization of the combination dyeing wastewater, an appreciable loss in color was observed when the treated samples were filtered through the Reeve Angel filter paper used to separate the powdered carbon from the solution (see Procedures, above). Even filtration of the control, i.e., no PAC added, resulted in an appreciable loss in color so that it was difficult to determine whether, and to what extent, the observed decolorization was due to the powdered carbon or to the filtration step used for separation of the carbon. In order to determine if the sample could be decolorized by activated carbon alone, a sample of crushed granular carbon was added to the

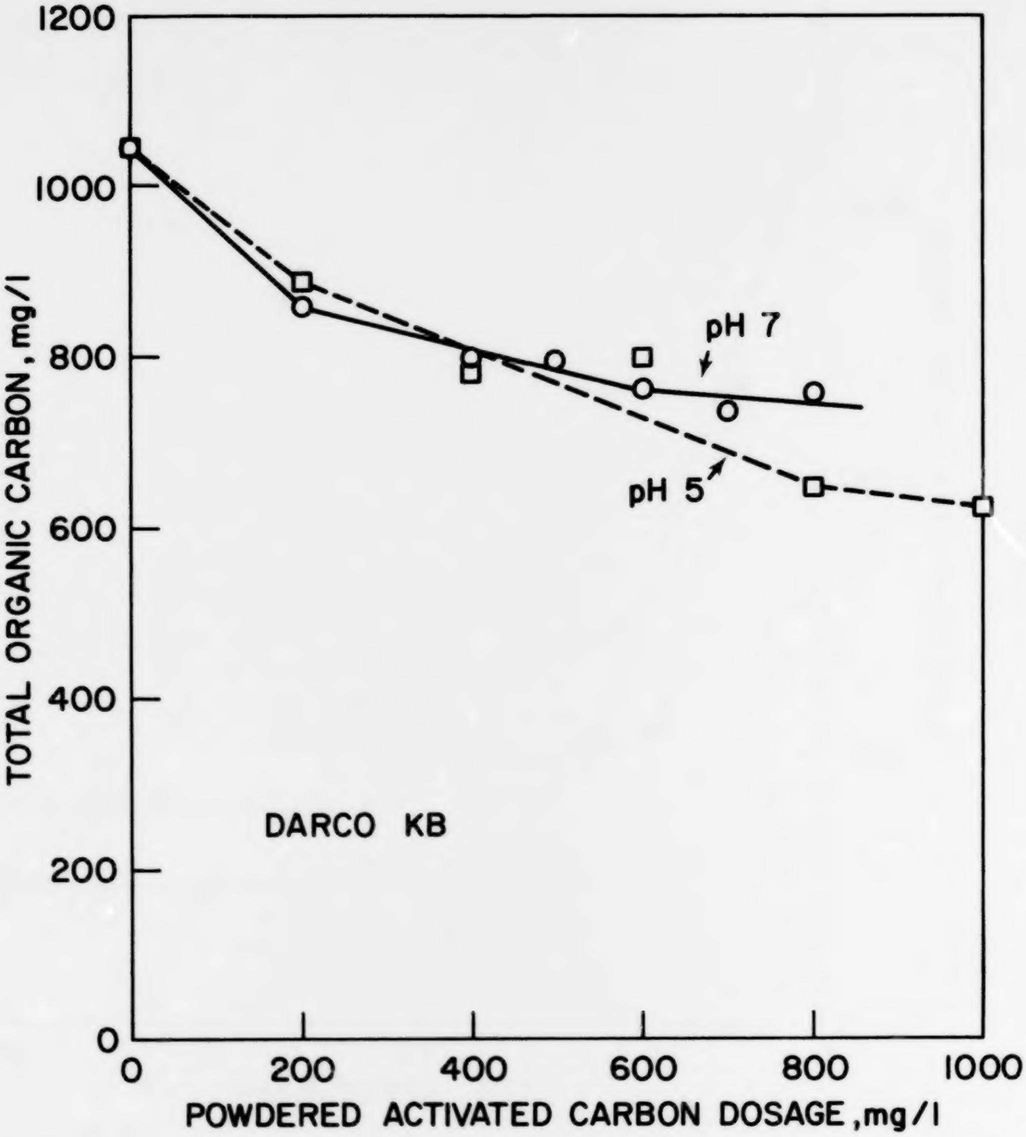

FIGURE 78. Dyeing Wastewater No. 18 (Basic Dyes on Polyester): Removal of Total Organic Carbon by Powdered Activated Carbon Adsorption

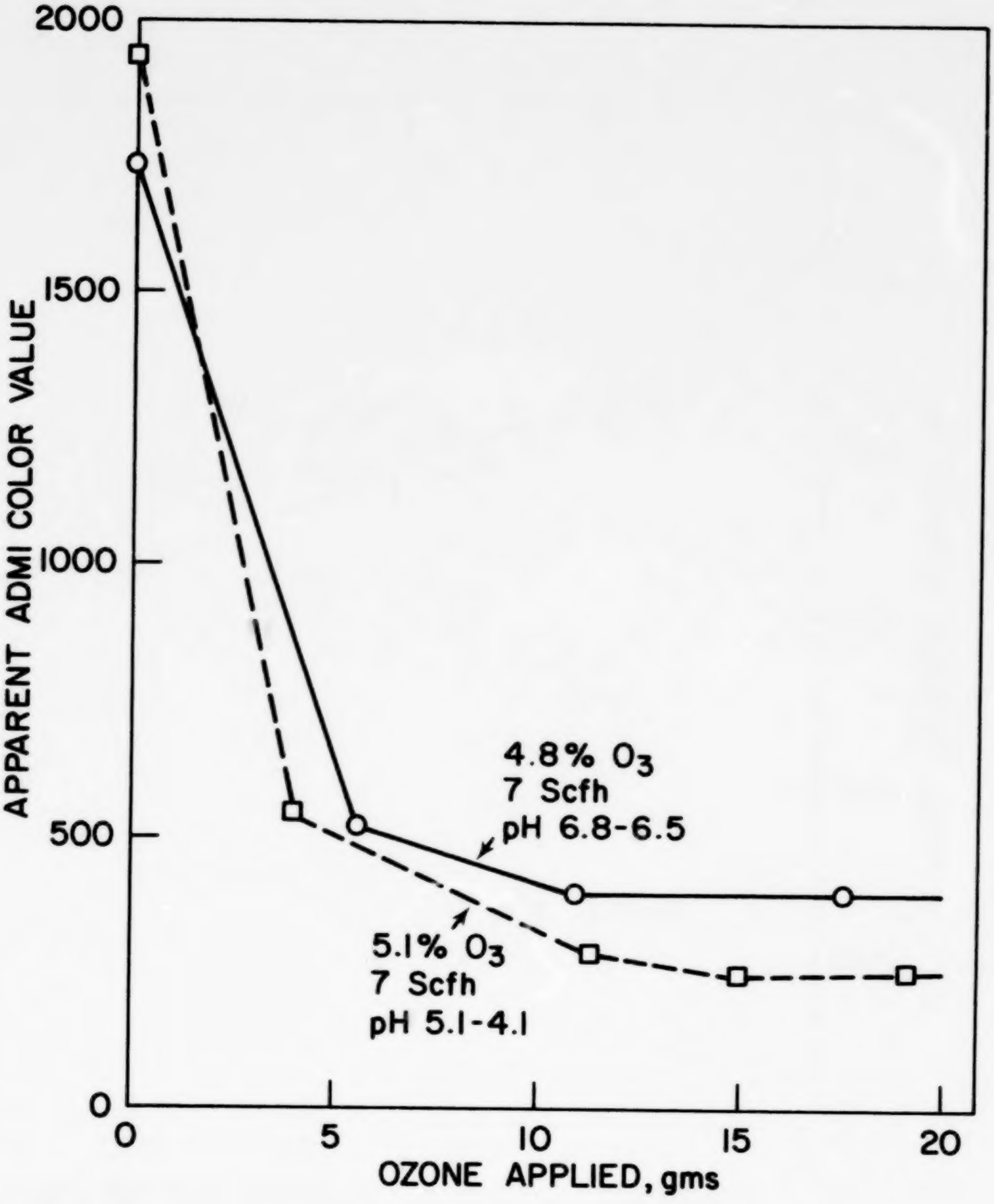

FIGURE 79. Dyeing Wastewater No. 18 (Basic Dyes on Polyester): Decolorization by Ozone

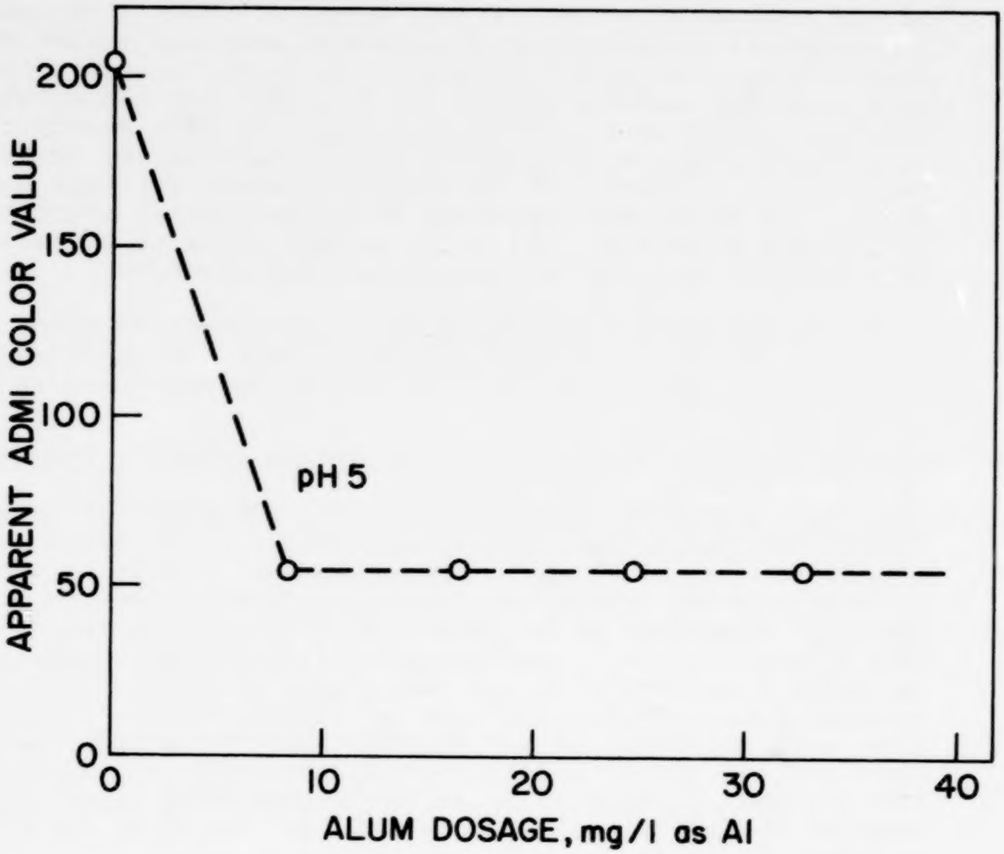

FIGURE 80. Dyeing Wastewater No. 19 (Disperse, Acid and Basic Dyes on Polyamide Carpet): Color Removal by Alum Coagulation

wastewater and mixed in the same fashion as the powdered carbon but separation was achieved by simple sedimentation of the coarser granular carbon (Darco HD-3000). No reduction in color was observed for the crushed granular carbon at doses up to 1000 mg/l. It should be noted, however, that only a 60-min contact period was provided for the crushed granular carbon and such contact may have been insufficient to achieve complete adsorption. Nevertheless, if activated carbon were an effective decolorizing agent for this wastewater, one would have expected at least partial adsorption of the dye molecules, primarily at the exterior surface of the carbon. No such decolorization was observed.

Decolorization of the mixed dyeing wastewater by ozone is shown in Figure 81; 4 gms of ozone (about 670 mg/l) reduced the color to less than 100. No defoaming agent was required.

Dyeing Wastewater No. 20. Azoic Dye on Cotton - Exhaust

The azoic dyeing wastewater contained an appreciable concentration of highly-colored solids, with a suspended solids concentration of 387 mg/l. The suspended particles tended to settle quite readily on standing, however, so the physical-chemical treatability studies were conducted on the colored supernatant following sedimentation. (The ADMI color shown in Table 5 in Section V (an ADMI color value of 2415) is the soluble color after separation of the particles.) Alum and lime were not required for coagulation of the solids as they settled quite readily without the addition of chemicals. The residual soluble color of the supernatant could not be removed by Al(III) doses up to 125 mg/l at pH 7, or 800 mg/l of lime (pH 12.1).

Powdered activated carbon, however, effectively decolorized the residual supernatant as shown in Figure 82 and Table 65. Darco HD-3000 and Nuchars D-14 and D-16 were the most effective decolorizing carbons (see Table 65). HD-3000 was tested to determine the effect of pH on decolorization and the results are depicted in the insert in Figure 82. There appears to be a sharp break at about pH 6 to 7 and subsequent treatment at pH 6 was tested at various levels of HD-3000 as shown; 800 mg/l reduced the color to less than 100. TOC removal was marginal as shown in Figure 83. A parallel run with Nuchar D-16 at pH 6 gave comparable results to those with the HD-3000. (No tests were performed in which the powdered carbon was added prior to separation of the solids.)

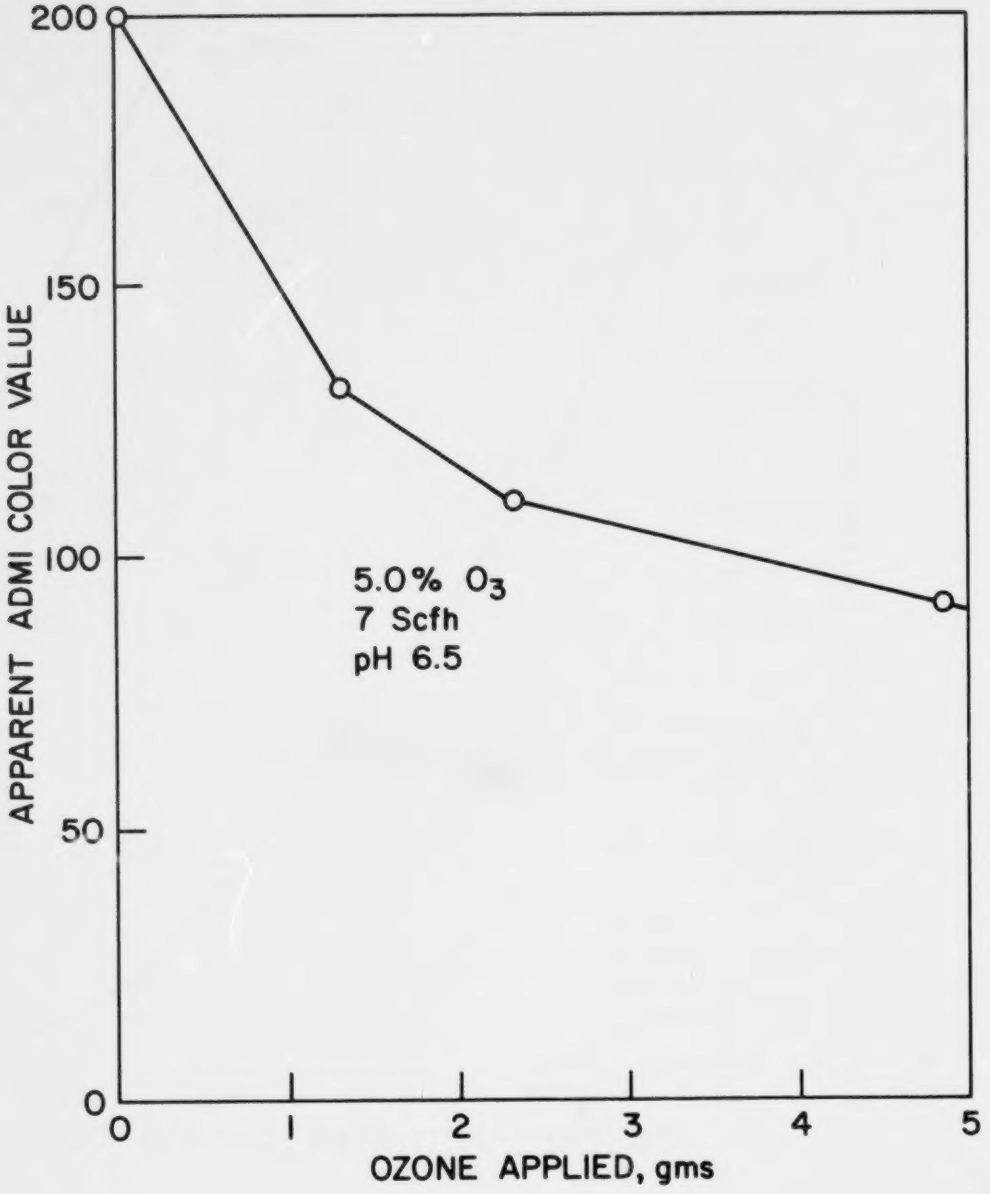

FIGURE 81. Dyeing Wastewater No. 19 (Disperse, Acid and Basic Dyes on Polyamide Carpet): Decolorization by Ozone

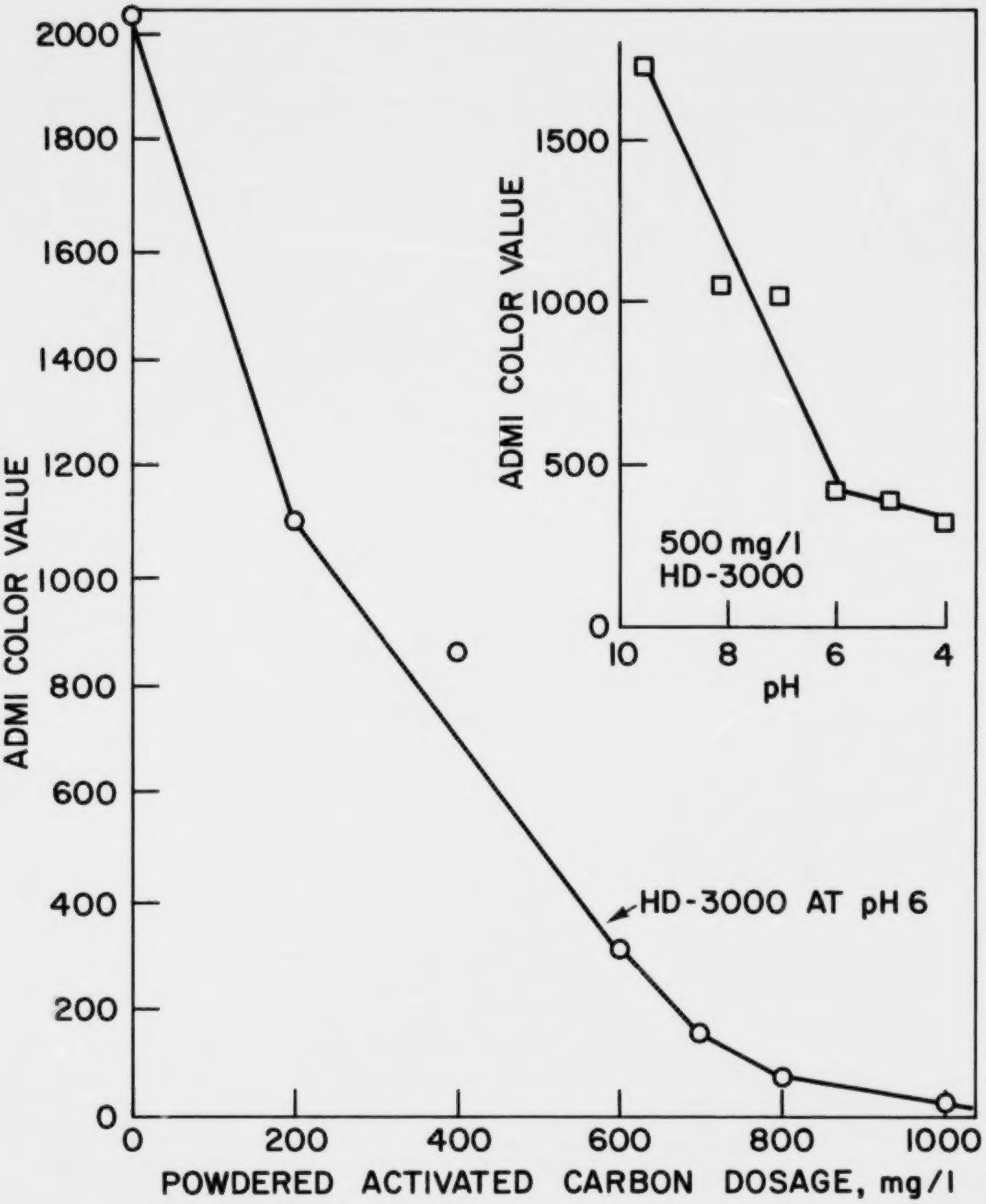

FIGURE 82. Dyeing Wastewater No. 20 (Azoic Dye on Cotton): Color Removal by Powdered Activated Carbon Adsorption

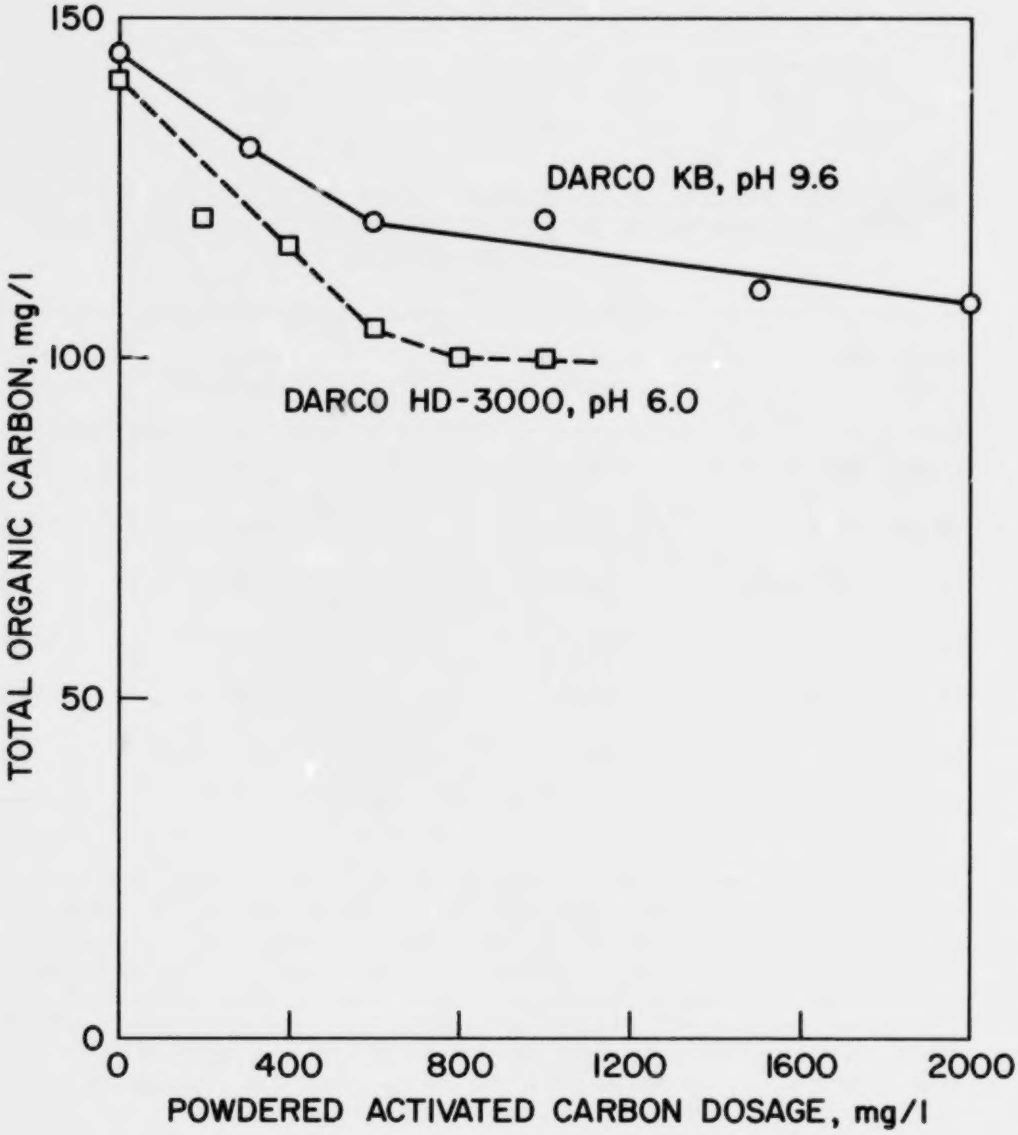

FIGURE 83. Dyeing Wastewater No. 20 (Azoic Dye on Cotton): Removal of Total Organic Carbon by Powdered Activated Carbon

TABLE 65. EFFECT OF DIFFERENT TYPES OF POWDERED ACTIVATED CARBONS ON TREATMENT OF DYEING WASTEWATER NO. 20 (AZOIC DYES ON COTTON)

Type of PAC	Dosage, mg/l	pH	TOC, mg/l	ADMI color
DARCO KB	1000	9.4	114	499
DARCO HDB	1000	9.6	108	645
DARCO HD-3000	1000	9.6	104	335
HYDRODARCO C	1000	9.6	121	1332
NUCHAR D-14	1000	9.2	105	397
NUCHAR D-16	1000	9.0	107	356

For the ozonation treatability study, the total azoic wastewater, including the solids, was suspended in the reactor and treated by ozone with the results shown in Figure 84. Following an initially rapid decolorization of the sample by 12 gms of ozone (2 gm/l) to an ADMI color value of 250, the continued application of ozone was relatively inefficient in decolorizing the waste further. Although the waste was eventually decolorized to less than 100, very large quantities of ozone were required (approximately 10 gms/l).

SUMMARY

Table 66 summarizes the results of the physical-chemical treatability studies for the twenty dyeing systems investigated. The results are discussed along with the biological treatability results in Section VIII.

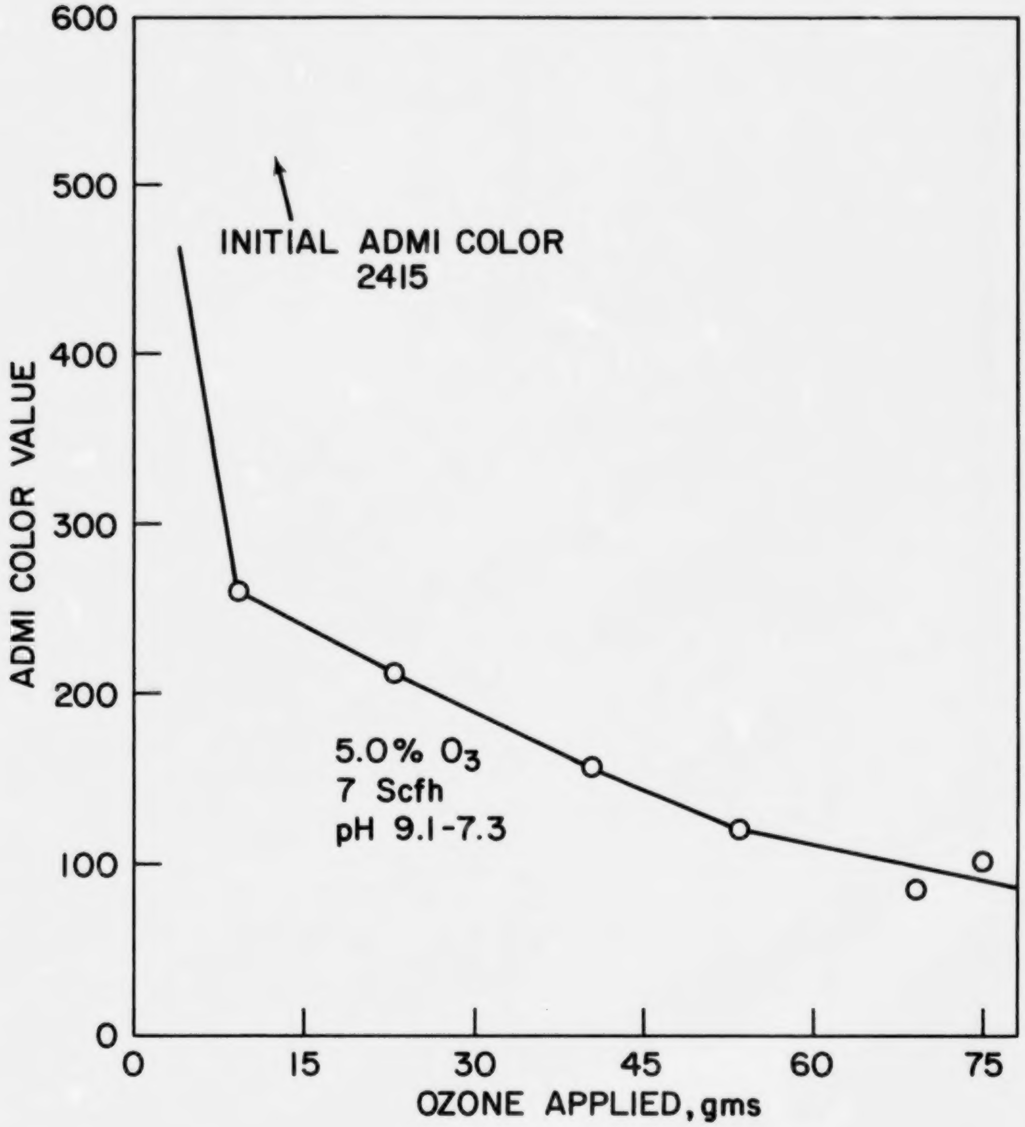

FIGURE 84, Dyeing Wastewater No. 20 (Azoic Dye on Cotton): Decolorization by Ozone

TABLE 66. SUMMARY OF PHYSICAL-CHEMICAL TREATABILITY STUDIES

Dyeing Wastewater No.	Dye Class	Substrate	Color	TOC, mg/l	Lime
1	Vat	Cotton	1910	265	1000 mg/l reduced color to 350, TOC to 210
2	1:2 Metal Complex	Polyamide	370	400	1000 mg/l reduced color to 230, no reduction of TOC
3	Disperse	Polyester	315	300	no change in color or TOC up to 1000 mg/l
4	After-Copperable Direct	Cotton	525 (1280[a])	135	200 mg/l reduced apparent ADMI color to 120, little change in TOC
5	Reactive	Cotton	3890	150	no effect on color or TOC up to 3 gms/l
6	Disperse	Polyamide Carpet	100	130	200 mg/l reduced color to 50, little removal of TOC
7	Acid/Chrome	Wool	3200	210	No color removal, some TOC removal up to 2000 mg/l
8	Basic	Polyacrylic	5600 (12,000[a])	255	2000 mg/l ineffective for color or TOC reduction

---

[a] Prefiltration step omitted in ADMI color analysis.

TABLE 66. SUMMARY OF PHYSICAL-CHEMICAL TREATABILITY STUDIES (continued)

Dyeing Wastewater No.	Alum	PAC	Ozone	Other	Comments
1	140 mg/l (pH 6.3) reduced color to 100, TOC to 80	no visible color change up to 4 gms/l (pH 11) of Darco HD-3000	------------------------	------	---------
2	160 mg/l (pH 6.3) reduced color to 230, no reduction of TOC	900 mg/l Nuchar D-16 reduced color to 100, TOC to 320 (at pH 6.8)	Efficient decolorization: 130 mg O_3/l reduced color to 100; no change in TOC; slight drop in pH	-------	----------
3	60 mg/l (pH 5) reduced color to 45, TOC to 175; pH 5 better than pH 6, 7	little change in color up to 1200 mg/l of Nuchar D-16 (pH 7.8)	Poor decolorization: 6 gms O_3/l reduced color to 180; lag period; no change in TOC; small drop in pH	Fe(III) at 260 mg/l reduced color to 50, TOC to 130; pH 5 better than pH 6; underdosed samples yield high turbidity and red Fe(III) color	------------
4	16 mg/l (pH 6) reduced apparent ADMI color to 80, little change in TOC	---------------------	Good decolorization: apparent color reduced to 60 by application of 500 mg O_3/l; no change in pH or TOC	---------------------	Turbid sample, most of color associated with suspended particles
5	160 mg/l (pH 5) reduced color to 635, TOC to 60; higher doses showed no improvement	2000 mg/l HD-3000 (pH 3.5) reduced color to 100, TOC to 20; pH 3.5 better than pH 7 or 10.7	Good decolorization: color reduced to 100 by 1.0 gm/l O_3; reduction more rapid at alkaline pH of raw waste (10.7) than at pH 8 or 2; no removal of TOC	---------------------	-------------
6	30 mg/l (pH 7) reduced color to less than 50, TOC removal small	200 mg/l HD-3000 reduced color to 65; 1000 mg/l reduced TOC to 60	-------------------------	---------------------	Very low initial color
7	No color removal, some TOC removal up to 160 mg/l at pH 7	4 gms/l HD-3000 (pH 4.2) reduced color to 75; acidic pH most effective; small TOC removal	-------------------------	Treatment by acidification with H_2SO_4 to pH 3, Fe(II) addition, neutralization to pH 7 with lime, floccn. and settling; 180 mg/l Fe(II) reduced color to 150, TOC to 130 with 10 min. acid contact	37.5 mg/l total Cr (assumed to Cr(VI))
8	315 mg/l ineffective for color or TOC reduction at pH 7	1000 mg/l Nuchar D-16 (or 2000 mg/l HD-3000) reduced apparent color to less than 100; pH 4.5 optimal; TOC reduced to 150	Good decolorization, but apparent color leveled off at about 200 at 2 gms/l O_3; noticeable lag prior to decolorization; rxn. more rapid at pH 4.2 than at neutral pH; no change in TOC but BOD increased after O_3 application	---------------------	Appreciable loss in color using ADMI procedure with prefiltration by Celite

TABLE 66. SUMMARY OF PHYSICAL-CHEMICAL TREATABILITY STUDIES (continued)

Dyeing Wastewater No.	Dye Class	Substrate	Color	TOC, mg/l	Lime
9	Disperse	Polyester Carpet	215 (315[a])	240	1000 mg/l reduced apparent color to 130, TOC to 190
10	Acid	Polyamide	4000	315	1000 mg/l reduced color to 2150, no reduction of TOC
11	Direct	Rayon	12,500	140	3 gms/l gave no appreciable color or TOC removal
12	Direct Developed	Rayon	2730	55	400 mg/l reduced color to 300, TOC to 30; higher doses gave no improvement
13	Disperse, Acid, Basic	Polyamide Carpet	210 (720[a])	130	no apparent color reduction up to 4 gms/l
14	Disperse	Polyester	1245	360	1000 mg/l gave no reduction in color or TOC
15	Sulfur	Cotton	1450	400	500 mg/l reduced color to 100, no effect on TOC, floc did not settle well
16	Reactive	Cotton	1390	230	1000 mg/l gave no apparent color reduction

---

[a] Prefiltration step omitted in ADMI color analysis.

TABLE 66. SUMMARY OF PHYSICAL-CHEMICAL TREATABILITY STUDIES (continued)

Dyeing Wastewater No.	Alum	PAC	Ozone	Other	Comments
9	150 mg/l (pH 5) reduced apparent color to 80, TOC to 110; very light floc	2000 mg/l Nuchar D-16 reduced TOC to 75 but no change in color	Decolorization relatively slow; apparent lag; acidification to pH 4 more rapid than at pH 7; apparent color reduced to 70 by 4 gms/l O_3; no change in TOC but BOD increased with treatment	----------------	High turbidity wastewater, some loss of color using ADMI procedure with Celite
10	160 mg/l (pH 7) reduced color to 2150, TOC to 160	1000 mg/l Darco KB or Nuchar D-14 reduced color to 260, TOC to 175; pH 5.1 optimal; cannot get color below 200 even at higher doses	Poor decolorization: color reduced to 400 by 4 gms/l O_3; pH dropped dramatically (to 3.5) by ozonation; no change in TOC but BOD increased	----------------	------------
11	30 mg/l (pH 5) reduced color to 2000, TOC to 30; color could not be reduced by higher alum doses	2 gms/l gave no color or TOC removal at pH 6.6	Poor decolorization: 4.5 gms/l O_3 reduced color to 1150; pH dropped during treatment; small TOC reduction but BOD increased	Two step treatment: 30 mg/l alum at pH 5, 600 mg/l Nuchar D-14 reduced color to 35, TOC to less than 10	------------
12	8 mg/l (pH 5) reduced color to 300, TOC to 30; no improvement at higher doses	1000 mg/l (pH 3.1) gave no color reduction	Good color reduction: 3.5 gms/l O_3 reduced color to <100; no apparent pH effect; small TOC reduction	Two step treatment: 8 mg/l alum at pH 5, 200 mg/l Nuchar D-14 reduced color to 100, TOC to 5	------------
13	No apparent color reduction up to 160 mg/l	500 mg/l Darco KB (pH 3) reduced apparent color to 40, TOC to 50; acid pH best	Good decolorization: apparent color reduced to 100 by 1.3 gms/l O_3; no effect of pH; no TOC reduction	------------------	------------
14	65 mg/l (pH 5) reduced color to 230, TOC to 130; no improvement at higher doses	1000 mg/l (pH 3) reduced color to only 500; little TOC removal	Poor decolorization: 3.5 gms/l O_3 reduced apparent color to 400; defoamer required; small reduction in TOC	Two step treatment: 65 mg/l alum at pH 5 + Nuchar D-14 up to 2 gms/l could not get color below 200	------------
15	8 mg/l reduced color to less than 100, no effect on TOC; floc settled poorly	1000 mg/l (pH 3.9) gave no apparent color reduction	Color reduced to 150 by 6.0 gms/l O_3; no apparent pH effect; defoamer required; no change in TOC	17 mg/l Fe(III) reduced color to 100 at pH 7 with good-settling floc	Sample extremely foamy, scum layer formed on all treated samples
16	160 mg/l (pH 7) gave no apparent color reduction	1700 mg/l Hydrodarco B (pH 6) reduced color to less than 50, TOC to 140; pH 6 optimal	Good decolorization: color reduced to less than 100 with 1.2 gm/l O_3; reaction more efficient at acidic pH; no change in TOC	------------------	-------------

TABLE 66. SUMMARY OF PHYSICAL-CHEMICAL TREATABILITY STUDIES (continued)

Dyeing Wastewater No.	Dye Class	Substrate	Color	TOC, mg/l	Lime
17	Vat, Disperse	Polyester/ Cotton	365 (1100[a])	350	no floc formation or color removal up to 1000 mg/l
18	Basic	Polyester	1300 (2040[a])	1120	no apparent color reduction up to 1000 mg/l
19	Disperse, Acid, Basic	Polyamide Carpet	<50 (190[a])	160	no apparent color reduction up to 1000 mg/l
20	Azoic	Cotton	2415	170	800 mg/l had no effect on supernatant color

---

[a] Prefiltration step omitted in ADMI color analysis.

TABLE 66. SUMMARY OF PHYSICAL-CHEMICAL TREATABILITY STUDIES (continued)

Dyeing Wastewater No.	Alum	PAC	Ozone	Other	Comments
17	50 mg/l reduced apparent color to 80, small TOC removal; no adjustment of pH required; treated sample still foamed	1000 mg/l Darco KB at pH 3.3 reduced apparent color to 325	Poor decolorization: 9 gms/l O_3 reduced apparent color to 400; defoamer required; slight TOC reduction	-------------------	Appreciable loss in color by Celite filtration
18	No apparent color reduction up to 160 mg/l at pH 5	700 mg/l Darco KB (pH 5) reduced apparent color to 100; TOC reduced to 700; pH 6-7 optimal	Apparent color reduced to 300 by 2 gms/l O_3 but could not be reduced below 250; defoamer required; acidic pH better than neutral pH; no reduction in TOC	-------------------	Some color lost via Celite filtration, treated sample still foamed
19	8 mg/l (pH 7) reduced color to 50; no change in TOC	no apparent decolorization	Good decolorization to less than 100 by 500 mg/l O_3; TOC reduced slightly	-------------------	Very slight color; color removed easily at all interfaces, e.g., filters, Celite, $Al(OH)_3$
20	125 mg/l had no effect on supernatant color	800 mg/l of Darco HD-3000 or Nuchar D-16 at pH 6 reduced color of supernatant to 100; TOC removal slight; acid pH best	Efficient initial decolorization to 260 by 1.5 gms/l O_3 followed by slower decolorization to less than 100 by 11 gms/l O_3; defoamer required; no change in TOC	-------------------	Waste contained appreciable suspended solids concentration with color associated with particles; solids (and associated color) settled readily on standing

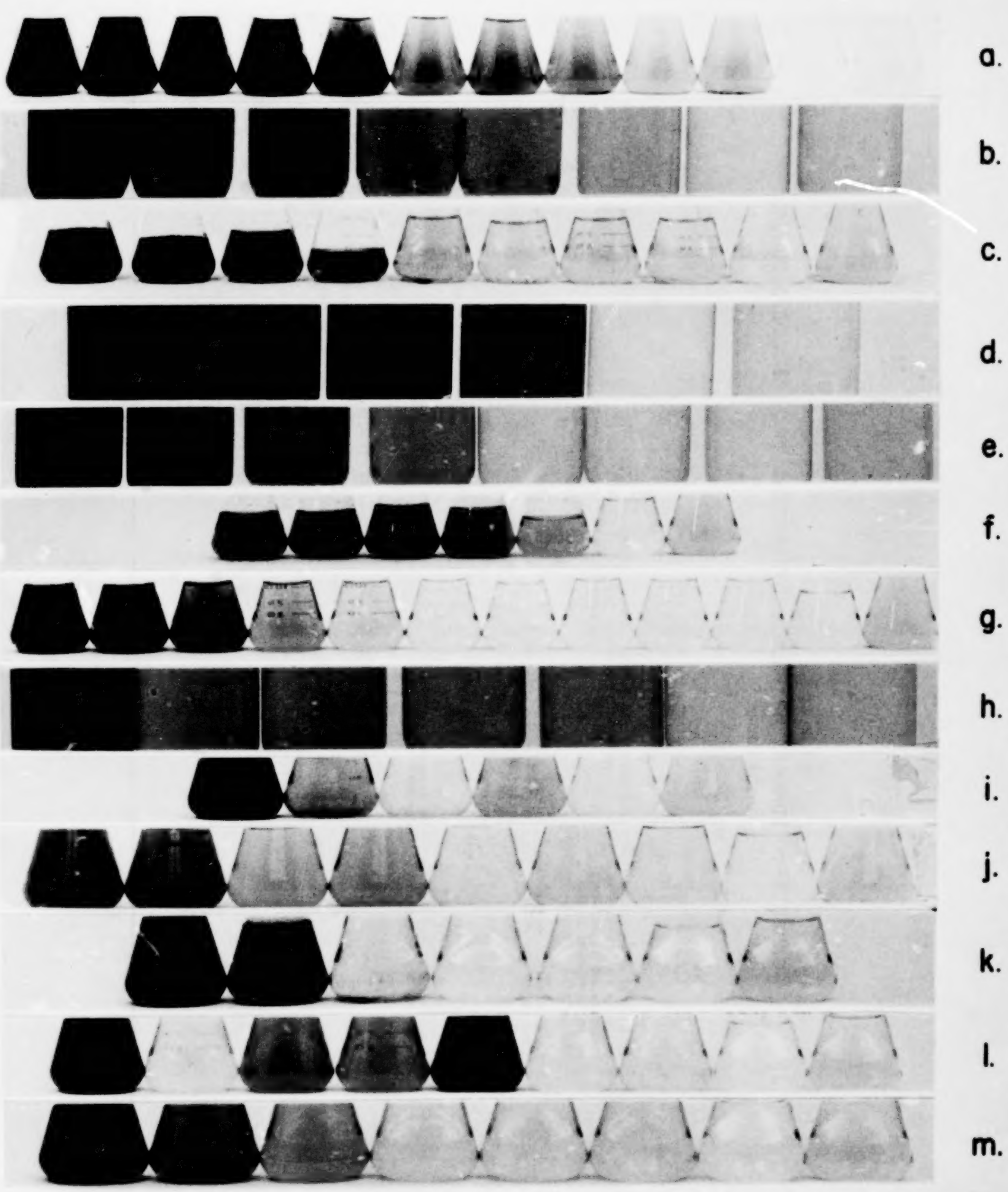
a.
b.
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FIGURE 85. Colored Photograph Showing Effect of Different Treatments on the Appearance of Representative Dyeing Wastewater

TABLE 67. LEGEND FOR FIGURE 85

a. Decolorization of Dyeing Wastewater No. 10 (Acid Dye on Polyamide) by Powdered Activated Carbon (Darco HD-3000 at pH 5.1)

Carbon Dosage, mg/l	0	200	400	600	800	1000	1200	1400	2000	4000	Pt-Co Standard	Pt-Co Standard
ADMI Color Value	4116	3140	2155	1828	832	289	289	251	210	228	50	300

b. Decolorization of Dyeing Wastewater No. 10 (Acid Dye on Polyamide) by Ozone

Ozone Applied, gms	0	5.0	7.3	12.3	17.8	22.8	Pt-Co Standard	Pt-Co Standard
pH	6.6	5.2	4.8	4.2	3.8	3.5	----	----
ADMI Color value	1790	815	680	560	480	420	50	300

TABLE 67. LEGEND FOR FIGURE 85 (continued)

c. Decolorization of Dyeing Wastewater No. 11 (Direct Dye on Rayon) by Alum Coagulation Alone (at pH 5) and by Two-Stage Treatment Consisting of Alum Coagulation (at pH 5) followed by Powdered Activated Carbon (Nuchar D-14)

Type of Treatment	Raw Dye Waste pH 6.6	Alum Only 16 mg/l	Alum Only 32 mg/l	Alum Only 161 mg/l	32 mg/l Alum, 400 mg/l PAC	32 mg/l Alum, 500 mg/l PAC	32 mg/l Alum, 600 mg/l PAC	32 mg/l Alum, 800 mg/l PAC	Pt-Co Standard	Pt-Co Standard
ADMI Color Value	12,500	7920	1975	1937	187	97	35	36	50	300

d. Decolorization of Dyeing Wastewater No. 11 (Direct Dye on Rayon) by Ozone

Ozone Applied gms	0	9.3	18.6	28.0	Pt-Co Standard	Pt-Co Standard
pH	9.5	4.3	3.6	3.4	----	----
ADMI Color Value	12,230	5550	3790	1145	50	300

TABLE 67. LEGEND FOR FIGURE 85 (continued)

e. Decolorization of Dyeing Wastewater No. 12 (Direct Developed Dye on Rayon) by Ozone

Ozone Applied gms	0	7.3	10.7	14.6	25.4	36.1	Pt-Co Standard	Pt-Co Standard
pH	2.8	2.7	2.7	2.7	2.6	2.6		
ADMI Color Value	1725	1800	1380	635	210	210	50	300

f. Decolorization of Dyeing Wastewater No. 13 (Disperse, Acid, and Basic Dyes on Polyamide Carpet) by Different Types of Powdered Activated Carbons (800 mg/l at pH 6.6)

Type of PAC	Nuchar D-14	Nuchar D-16	Darco HDB	Darco HD 3000	Darco KB	Pt-Co Standard	Pt-Co Standard
Apparent ADMI Color Value	300	311	371	302	234	50	300

TABLE 67. LEGEND FOR FIGURE 85 (continued)

g. Decolorization of Dyeing Wastewater No. 13 (Disperse, Acid, and Basic Dyes on Polyamide Carpet) by Powdered Activated Carbon (Darco KB at pH 3.0)

Carbon Dosage mg/l	0 pH 3.0	0 pH 6.6	200	300	400	500	600	700	800	900	Pt-Co Standard	Pt-Co Standard
Apparent ADMI Color Value	830	750	306	175	97	38	32	22	32	25	50	300

h. Decolorization of Dyeing Wastewater No. 14 (Disperse Dye on Polyester) by Ozone

Ozone Applied, gms	0	4.6	7.2	13.5	21.9	Pt-Co Standard	Pt-Co Standard
pH	9.7	6.7	6.6	6.2	6.1	--	---
ADMI Color Value	1180	377	366	325	280	50	300

TABLE 67. LEGEND FOR FIGURE 85 (continued)

i. Decolorization of Dyeing Wastewater No. 15 (Sulfur Dye on Cotton) by Coagulation

Type of Treatment	Raw Dye Waste	400 mg/1 Lime	800 mg/1 Lime	17 mg/1 Alum, pH 5	Pt-Co Standard	Pt-Co Standard
ADMI Color Value	1450	122	48	63	50	300

j. Decolorization of Dyeing Wastewater No. 16 (Reactive Dye on Cotton) by Powdered Activated Carbon (Darco HDB at pH 6.0)

Carbon Dosage, mg/1	0	500	1000	1300	1500	1600	1700	Pt-Co Standard	Pt-Co Standard
ADMI Color Value	1400	705	341	203	106	83	42	50	300

TABLE 67. LEGEND FOR FIGURE 85 (continued)

k. Decolorization of Dyeing Wastewater No. 17 (Disperse and Vat Dyes on Polyester/Cotton) by Alum Coagulation

Alum Dosage mg/1	0	32	40	48	55	Pt-Co Standard	Pt-Co Standard
pH	10.9	7.5	6.6	6.1	5.6	--	---
Apparent ADMI Color Value	1189	1059	239	71	58	50	300

l. Decolorization of Dyeing Wastewater No. 18 (Basic Dyes on Polyester) by Different Types of Powdered Activated Carbons (400 mg/1 at pH 5.0)

Type of PAC	Raw Dye Waste	Darco KB	Darco HDB	Darco HD 3000	Hydro Darco C	Nuchar D-14	Nuchar D-16	Pt-Co Standard	Pt-Co Standard
Apparent ADMI Color Value	1400	263	1611	1631	1674	168	129	50	300

TABLE 67. LEGEND FOR FIGURE 85 (continued)

m. Decolorization of Dyeing Wastewater No. 18 (Basic Dyes on Polyester) by Powdered Activated Carbon (Nuchar D-16 at pH 5.0)

Carbon Dosage, mg/l	0	100	200	300	400	500	Pt-Co Standard	Pt-Co Standard
ADMI Color Value	1282	922	395	88	58	63	50	300

SECTION VIII

DISCUSSION OF TREATABILITY RESULTS

BIOLOGICAL TREATABILITY

Objectives of this research were to compare the biological treatability of the twenty dyeing wastewaters and to determine the effect on nitrification. These studies were performed at laboratory scale, using procedures similar to those employed for determining long term BOD; the wastewaters tested were generated in well-defined standard dyeing operations. These results, therefore, are intended only as a guide in biological treatability of dyeing wastewaters, and further experimentation will be required to generate the information for design of plant-scale wastewater treatment systems.

Tables 68 and 69 summarize results from laboratory-scale studies of biological treatability of the dyeing wastewaters. The results show that at the 10% strength, $\geq$ 90% of the soluble BOD_5 was removed in 18 of the 20 cases, and at full strength, $\geq$ 90% removals were achieved in 15 of the 20 cases. Only in one case, no. 5, were BOD removals less than 50%. Dyeing wastewater no. 5 inhibited biological activity at the 10% and 100% strengths. It was also not possible to maintain a bench-scale activated sludge system when this wastewater was present in the feed. Results from the lowest strength (1%) are hard to interpret since it was not possible to perform BOD's. The initial TOC levels were low at this strength; however, removal of most of the TOC possibly indicates that some biological treatment occurred. Dyeing wastewater no. 5 contained an unusually high level of chlorides (9800 mg/l) and more chloride was added when the pH was lowered with HCl from 11.2 to 7 for the biological treatability studies. Due to other sodium salt components in the dyebath, it is conceivable that sodium inhibition might be involved. Since inhibitory effects were noted at the 10% strength, at which the chloride and other dissolved solids were diluted by tenfold, it would seem doubtful that the dissolved solids concentration was responsible for the inhibition. Many common bacteriological media contain 5 g of NaCl per liter, and some industrial wastewater treatment systems are known to operate successfully at chloride levels of ~17,000 mg/l.

In the case of wastewater no. 5, the dyeing process also involved addition of an anti-reducing agent, sodium m-nitro-

TABLE 68. EFFECT OF BIOLOGICAL TREATMENT ON BOD, TOC, AND COLOR REMOVAL FROM DYEING WASTEWATERS

	A. BOD_5 REMOVAL			B. TOTAL ORGANIC CARBON REMOVAL			C. COLOR REMOVAL[a]		
	Removal, %			Removal, %			Removal, %		
DILUTION	<50	50-89	≥90	<50	50-89	≥90	<50	50-89	≥90
10%	5	17	1, 2, 3, 4, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 18, 19, 20		1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 13, 14, 16, 17, 20	12, 15, 18, 19	3, 4, 5, 6, 7, 10, 11, 12, 14, 16, 17, 18, 20	1, 2, 8, 13, 15	
100%	5	8, 13, 17, 18	1, 2, 3, 4, 6, 7, 9, 10, 11, 12, 14, 15, 16, 19, 20	3, 5, 10, 11, 12, 14	1, 2, 4, 6, 7, 8, 9, 13, 16, 17, 18, 19, 20	15	1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 16, 17, 18	13, 15, 20	

[a] No. 7 was not measured at the 100% level; the color at 10% strength was too low for analysis in the case of No. 9, and for No. 19 the color was too low at both the 10% and the 100% strengths.

TABLE 69. EFFECT OF DYEING WASTEWATERS ON NITRIFICATION

Set	Inhibition[a,b]		
	None	Moderate	Marked
A-10	1,2,5,6,7,9, 11,12,13,15, 16,17,18,19	3,14	4,8,10
B-10	2,6,9,11,13, 15,16,17,18, 19	----	1,3,4,5,7,8, 10,14
A-100	6,11	16	1,3,4,5,7,8, 9,10,13,14, 15,17,18,19
B-10	6,16	9,11,13	1,3,4,5,7,8, 10,14,15,17, 18,19

[a] None -- $\geq$50% of initial TKN as NO_2+NO_3-N (final)

Moderate -- 20-49% of initial TKN as NO_2+NO_3-N (final)

Marked -- <20% of initial TKN as NO_2+NO_3-N (final)

[b] No data for no. 2 at 100%; for no. 12 at B-10 and at 100%; no data for no. 20.

benzene sulfonate, but this agent was also employed in dyeing wastewater no. 16, a wastewater which was readily treatable. The reactive red dye used in dyeing wastewater no. 5 is therefore suspect. Further studies with the dye alone might reveal whether or not it inhibits exertion of BOD.

Overall, it is reasonable to conclude that in 19 of 20 cases, presence of dyes in dyeing wastewaters did not interfere with the removal of BOD.

TOC was generally removed to a lesser degree than the BOD (Table 68). In the majority of cases, 50-89% removals were achieved in seeded flasks. In Table 70 BOD_5/TOC ratios are shown before and after treatment. The BOD_5/TOC ratios in domestic wastewaters are generally ~1.62 in the raw waste, ~0.47 in the effluent.[1] It should be noted that the BOD test is a test of biochemical oxygen consumption and that the test may not reflect the presence of organic compounds which are partially or totally resistant to biodegradation. On the other hand, the TOC test recovers all the organic carbon, regardless of its biodegradability. Since biological treatment removes biodegradable organics, refractory organic carbon will account for a larger portion of the TOC in the effluent than in the raw wastewater. Thus, the BOD_5/TOC ratio will be lower in the effluent. Table 70 readily illustrates the lowering of the ratio by treatment. In the raw wastewaters the ratios are, with only 4 exceptions, lower than that characteristic of domestic sewage.

In the treated wastewaters the ratios were generally lower than for treated domestic wastewaters and in many cases were 0.0, indicating that the refractory component accounted for nearly all of the remaining TOC.

Because of the lack of precision of the BOD test and because of the very low residual BOD_5 levels in many cases, the information in Table 68 must be interpreted cautiously. However, it is apparent that the majority of the wastewaters contain organics which are only partially degraded even after 21-day culture with acclimated organisms. This possibly indicates that these organics would not be oxidized in biological wastewater treatment systems.

Under the conditions tested, biological treatment appears to be inadequate for color removal. The raw wastewater color levels were low in dyeing wastewater no. 19. In the remaining 19 cases, color removals of less than 90% were achieved, and in the large majority of cases, less than 50% removal was achieved (Table 68). In some cases, soluble color increased during treatment.

The effect of dyeing wastewaters on nitrification (Table 69) warrants further investigation. In a previous study,[2] several dyes were shown to interfere with nitrification in dye-supplemented domestic wastewater. For many years, the dye methylene blue has been known to inhibit nitrification.[3,4]

In the degradation of organic nitrogen compounds, ammonia is usually produced by microbiological processes referred to as "ammonification." Nitrification, a microbiological process, involves the oxidation of the ammonia nitrogen to nitrite and subsequently to nitrate. Because of the toxicity of ammonia to fish and because of the nitrogenous oxygen demand which would be exerted if ammonia were discharged to a sur-

TABLE 70. EFFECT OF BIOLOGICAL TREATMENT ON BOD_5/TOC RATIOS IN DYEING WASTEWATERS WITH ACCLIMATED SEED

Dyeing Wastewater	Set	BOD_5/TOC Initial	BOD_5/TOC Final
1	B-1	1.4	---
	B-10	1.1	<0.1
	B-100	0.9	0.0
2	B-1	0.8	---
	B-10	0.6	0.3
	B-100	1.2	0.03
3	B-1	1.7	0.5
	B-10	1.4	0.1
	B-100	1.0	0.0
4	B-1	1.2	---
	B-10	1.0	0.7
	B-100	0.8	0.2
5	B-1	---	---
	B-10	---	---
	B-100	---	---
6	B-1	1.4	0.5
	B-10	1.2	<0.1
	B-100	0.7	0.0
7	B-1	0.8	---
	B-10	1.0	0.2
	B-100	0.9	0.0
8	B-1	1.0	0.2
	B-10	1.4	0.4
	B-100	0.8	0.7
9	B-1	---	---
	B-10	1.0	<0.1
	B-100	0.7	0.0
10	B-1	1.2	0.5
	B-10	1.0	<0.1
	B-100	0.7	0.0

TABLE 70. EFFECT OF BIOLOGICAL TREATMENT ON BOD_5/TOC RATIOS IN DYEING WASTEWATERS WITH ACCLIMATED SEED (continued)

Dyeing Wastewater	Set	BOD_5/TOC Initial	BOD_5/TOC Final
11	B-1	1.7	<1.0
	B-10	1.1	<0.1
	B-100	0.3	0.0
12	B-1	1.2	---
	B-10	1.2	0.3
	B-100	0.6	0.0
13	B-1	1.2	<0.5
	B-10	1.1	0.8
	B-100	0.8	0.3
14	B-1	1.0	0.1
	B-10	0.7	0.0
	B-100	0.4	0.1
15	B-1	0.8	1.4
	B-10	1.7	<1.0
	B-100	2.0	<0.0
16	B-1	1.0	<1.0
	B-10	1.0	<0.2
	B-100	1.0	0.1
17	B-1	1.4	1.7
	B-10	---	<0.5
	B-100	---	0.4
18	B-1	1.4	<0.2
	B-10	1.7	<0.1
	B-100	1.4	0.8
19	B-1	1.0	---
	B-10	1.1	<1.0
	B-100	1.0	0.0
20	B-1	0.8	<0.5
	B-10	0.9	0.5
	B-100	1.2	0.0

face water, there is currently interest in setting effluent standards which require low levels of ammonia nitrogen. One of the processes for removing ammonia is biological nitrification, which can be achieved in extended aeration systems, or in specially designed activated sludge or trickling filter systems. In the presence of certain of the dyeing wastewaters tested little or no conversion of total Kjeldahl nitrogen (organic + ammonia nitrogen) to nitrate was achieved. Little or no nitrate formation was observed with wastewaters nos. 3, 4, 8, 10, and 14 at 10% strength; at full-strength, little or no nitrate formation occurred with nos. 1, 5, 7, 15, and 17. The data for no. 19 were difficult to interpret, but no increase in nitrate occurred. No data on the final concentrations of nitrogen forms was available for no. 20. These observations indicate that either ammonification and/or nitrification failed to occur.

Computation of nitrogen balances, even for domestic wastewater, is difficult and often up to 20% of the nitrogen cannot be accounted for. The interference of the dyes with spectrophotometric analyses, even with standard addition techniques, also complicated interpretation of the final results. However, it seems reasonable to conclude that some component of a number of the wastewaters either interfered with nitrification or was resistant to ammonification. Studies of the effects of specific dyes on nitrification of domestic wastewater and of stream water are in progress.

PHYSICAL-CHEMICAL TREATABILITY

The purpose of this section is to compare the twenty dyeing wastewaters as to their treatability by physical-chemical techniques. The major emphasis is on decolorization while TOC removal is considered to be of secondary importance; TOC was removed quite readily by biological oxidative processes whereas color was difficult to remove by such processes, as demonstrated by the biological treatability results discussed above and by numerous textile plant experiences. Again, the reader is cautioned that the results were derived from a laboratory-scale, batch treatability analysis and are intended to serve only as a guide in selecting the most appropriate treatment method and chemical conditions for the full-scale treatment of real textile wastewaters.

Adsorption and Coagulation

Table 71 presents a summary of the adsorption and coagulation results showing the best means of decolorization for each of the twenty dyeing wastewaters sub-divided by dye class.

TABLE 71. COALGULATION AND ADSORPTION: BEST MEANS OF DECOLORIZATION BY DYE CLASS

Dye class	Dyeing no.	Substrate	ADMI color value	Best treatment
Vat	1	Cotton	1910	Alum coagulation
Disperse	3	Polyester	315	Alum coagulation
Disperse	6	Polyamide carpet	100	Alum coagulation
Disperse	9	Polyester carpet	315[a]	Alum coagulation
Disperse	14	Polyester	1245	Alum coagulation
Vat + disperse	17	Polyester/ cotton	1100[a]	Alum coagulation
Sulfur	15	Cotton	1450	Alum coagulation
Reactive	5	Cotton	3890	Carbon adsorption
Reactive	16	Cotton	1390	Carbon adsorption
Basic	8	Polyacrylic	12.000[a]	Carbon adsorption
Basic	18	Polyester	2040[a]	Carbon adsorption
Acid	10	Polyamide	4000	Carbon adsorption
Azoic	20	Cotton	2415	Carbon adsorption
1:2 metal complex	2	Polyamide	370	Carbon adsorption
Direct (after-copperable)	4	Cotton	1280[a]	Alum
Direct	11	Rayon	12,500	Alum + Carbon
Direct developed	12	Rayon	2730	Alum + Carbon
Disperse + acid + basic	13	Polyamide carpet	720[a]	Carbon adsorption
Disperse + acid + basic	19	Polyamide carpet	190[a]	Alum
Acid/chrome	7	Wool	3200	Fe(II)

---

[a] Prefiltration step omitted prior to ADMI color analysis.

(Treatability by chemical oxidation with ozone is considered in the next section.) The vat and disperse dyeing wastewaters and the one sulfur dyeing wastewater were decolorized most effectively by coagulation with aluminum and quite ineffectively, in general, by activated carbon adsorption. Ferric iron or other coagulants and flocculants (such as polyelectrolytes) could probably be used in place of alum, but the effectiveness of these alternative chemicals would have to be evaluated. In the case of Fe(III), some care must be exercised since underdosing the system with insufficient Fe(III) can result in a marked enhancement of the color due to the presence of the yellowish-brown colloidal ferric hydroxide as was observed for dyeing wastewater no. 3. Lime can also be used as a coagulant, but its effectiveness is limited to systems where there is an appreciable carbonate alkalinity to allow formation of $CaCO_3$. Lime was found to be effective in decolorizing wastes 6 and 9 (disperse dyes), 15 (sulfur dye), and 4 (after-copperable direct dye), and partially effective for wastes 1 (vat dye), 2 (1:2 metal complex dye), and 12 (direct-developed); it was ineffective in decolorizing the other systems, some of which were readily decolorized by alum, (e.g., wastes 3, 14, 17, 19).

Activated carbon adsorption proved to be an effective means of decolorizing the reactive, basic, acid, azoic, and 1:2 metal complex dyeing wastewaters. Correspondingly, coagulation with alum or lime was generally ineffective in decolorizing these wastes.

No specific statements can be made about the other dyeing wastewaters investigated as they consisted of either a mixture of dye classes (e.g., wastes 13 and 19) or required a combination of treatments, i.e., both coagulation and adsorption (e.g., wastes 11 and 12). The after-copperable direct dyeing wastewater (no. 4) was decolorized most effectively by coagulation with lime or alum since most of the color was associated with suspended particles which could be readily destabilized and aggregated by the coagulants. Dyeing wastewater no. 7 contained an acid dye and Cr(VI) and was decolorized most effectively by reduction of the highly-colored Cr(VI) with ferrous iron at low pH and subsequent neutralization with lime.

Table 72 shows the best treatment in terms of requisite alum dosage and the corresponding degree of decolorization and TOC removal for those wastes which were most treatable by coagulation. The "best" treatment was selected as that dosage of alum beyond which the decolorization curve (i.e., plot of residual color vs alum dosage) levels off (see Section VII).

TABLE 72. REQUISITE ALUM DOSAGES FOR BEST DEGREE OF DECOLORIZATION, AND CORRESPONDING REMOVALS OF TOTAL ORGANIC CARBON

Dye class	Dyeing no.	Substrate	Requisite alum dosage, mg/l as Al	Initial color value	Final color value	Initial TOC, mg/l	Final TOC, mg/l	TOC Reduction, %
Disperse	3	Polyester	60	315	45	300	170	43.3
Disperse	6	Polyamide carpet	30	100	50	130	110	15.4
Disperse	9	Polyester carpet	160	315[a]	80[a]	240	115	52.1
Disperse	14	Polyester	60	1245	230	360[b]	130	63.9
Vat	1	Cotton	80	1910	140	265[b]	115	56.6
Vat/Disperse	17	Polyester/ cotton	50	1100[a]	80[a]	350	300	14.3
Sulfur	15	Cotton	8	1450	80	400	345	13.8
Disperse/Acid/ Basic	19	Polyamide	8	190[a]	55[a]	160	135	15.6
After-copperable direct	4	Cotton	15	1280[a]	80[a]	135	100	25.9

[a] Prefiltration step omitted.

[b] Initial TOC for coagulation study appreciably less than TOC of raw fresh waste.

The TOC removals shown correspond to these same alum dosages. In all cases, alum was most effective in the pH range 5 to 6; pH control is mandatory for efficient coagulation by Al(III). The required doses vary for the different wastes over the range 8 to 160 mg/l as Al, and it is apparent that the requisite dosage is not correlated to the initial color value but depends more significantly upon the type of dye and the other components of the dyeing wastewater. The requisite alum dosage to achieve effective decolorization depends upon whether the dye bodies are suspended or dispersed as colloidal particles or whether they are present as dissolved species; if dissolved, the effectiveness of alum in removing them depends upon their affinity for the aluminum hydroxide surface compared to other dissolved components in the waste, e.g., phosphate, which compete for the adsorptive sites on the surface. For example, both dyeing wastewaters 3 and 9 were generated by dyeing polyester fabric with Disperse Yellow 42 and Disperse Blue 87 and both had the same initial color value of 315. Waste no. 3 resulted from dyeing a polyester texturized double knit while no. 9 resulted from the dyeing of a polyester tufted carpet; both dyeings were performed by atmospheric exhaust on the same dye beck and at the same liquor ratio (30:1). Many of the components of both dye baths were the same (e.g., complex diaryl sulfonate dispersing agents, ethylene oxide non-ionic detergents, polyphosphates, acetic acid, and sodium hydrosulfite) albeit in different amounts, but dyeing system no. 3 contained orthophenyl phenol as the carrier while dyeing system no. 9 contained biphenyl as the carrier. Comparison of the raw waste characteristics (see Section V) shows that waste no. 9 had a higher suspended solids concentration than waste no. 3 (101 mg/l versus 39 mg/l, respectively); the TOC of the wastes were similar (300 mg/l and 240 mg/l for wastes 9 and 3, respectively). Orthophenyl phenol is appreciably more soluble than biphenyl and it would appear that the difference in the suspended solids concentrations and therefore the different requisite chemical doses for these two wastes is attributable to the different carriers used in the dye bath. It is interesting to note also that waste no. 14, generated by the disperse dyeing of polyester yarn by the high-temperature exhaust method using trichlorbenzene as the carrier, resulted in a waste that was difficult to decolorize to the same extent as the other disperse-on-polyester dyeings. As shown in Figure 65, increased applications of alum were unable to decolorize the sample below 200 ADMI color units. The significance of the other components of the dye bath and the differences in the chemical properties of the dye molecules themselves cannot be underestimated with respect to their effect on the requisite coagulant dosages and the resulting degrees of decolorization.

A similar statement can be made regarding TOC removal as it is apparent from Table 72 that the percent removals of TOC are quite different for the different dyeing wastewaters, even for wastewaters generated by dyeings from the same class of dyes. It can be concluded, in general, that alum coagulation is not very effective in removing total organic carbon from the wastewaters investigated, percent reductions ranging from 13 to 64%.

Table 73 summarizes the requisite activated carbon doses for decolorizing those wastes which were most treatable by adsorption. Again, the "best" treatment was selected as that dosage of PAC beyond which the decolorization curve leveled off. Also indicated are the most effective types of carbon among those investigated for each of the wastes, and the optimum pH conditions for decolorization. The corresponding TOC removals are also shown. Again, as in the case of alum, it is apparent that there is no correlation between the initial color value and the requisite carbon dosage. This lack of correlation is due to the nature of the dyes and their chemical affinity for the carbon surface relative to their affinity for water (i.e., their solubility), and to competition between the dyes and other organic components of the dye bath for the carbon surface. Also, not much can be said about the effect of pH on the adsorption of the dyes; in general, the extent of adsorption of organics on carbon is known to increase with decreasing pH, but Table 73 does not support this generalization; no pattern is apparent. The adsorbability of the dyes on carbon as a function of pH appears to be specific for each of the systems studied. Even two dyes of the same class do not behave in the same fashion; Reactive Red 120 (waste no. 5) was more strongly adsorbed at acid pH (pH 3.5) while Reactive Red 40 (waste no. 16) was more strongly adsorbed at neutral pH (pH 6). Wastes 8 and 18, both containing basic dyes, also did not behave uniformly with respect to the effect of pH. This observed phenomenon is probably caused by the competitive adsorption of other dye bath components.

Figure 86 shows the effect of carbon dosage on the reactive and basic dyeing wastewaters, under the best conditions of adsorption tested, in an attempt to compare the relative adsorbabilities of these two dye classes on activated carbon. Carbon appears to decolorize the basic dyes more efficiently than the reactive dyes as less carbon was required to effect a given degree of decolorization. A more suitable means of comparison is to calculate, for each waste, the amount of color removed (dye adsorbed) by a given weight of carbon and to plot this quantity against the residual color (dye concentration) in accordance with the Langmuir adsorption model.

TABLE 73. REQUISITE POWDERED ACTIVATED CARBON DOSAGES FOR BEST DEGREE OF DECOLORIZATION, AND CORRESPONDING REMOVALS OF TOTAL ORGANIC CARBON

Dye class	Dyeing no.	Substrate	Requisite PAC dosage, mg/l	Most effective type of PAC[a]	Most effective pH	Initial color value	Final color value	Initial TOC, mg/l	Final TOC, mg/l	TOC Reduction, %
Reactive	5	Cotton	2500	HD-3000[b]	3.5	3,890	25	150[d]	20	86.7
Reactive	16	Cotton	1700	HDB, KB	6	1,390	50	230	140	39.1
Basic	8	Polyacrylic	1000	KB, D-14, D-16	4.5	12,000[c]	100[c]	255	140	45.1
Basic	18	Polyester	400	KB, D-14, D-16	7	2,040[c]	100[c]	1120	800	28.6
Acid	10	Polyamide	1000	KB, HDB, D-14, D-16	5.1	4,000	260	315	175	44.4
Azoic	20	Cotton	800	D-14, D-16, HD-3000	4	2,415	100	170	135	20.6
Acid (1:2 Metal Complex)	2	Polyamide	900	D-16[b]	6.8[b]	370	100	400	325	18.8
Disperse/ Acid/Basic	13	Polyamide Carpet	500	KB	3	720[c]	40[c]	130	50	61.5

[a] Carbons tested were DARCO HDB, HD-3000, KB, S-51, HYDRODARCO C, and NUCHAR D-14, D-16.
[b] Only one type of carbon or one pH tested.
[c] Prefiltration step omitted.
[d] Initial TOC for adsorption study appreciably less than TOC of raw fresh waste.

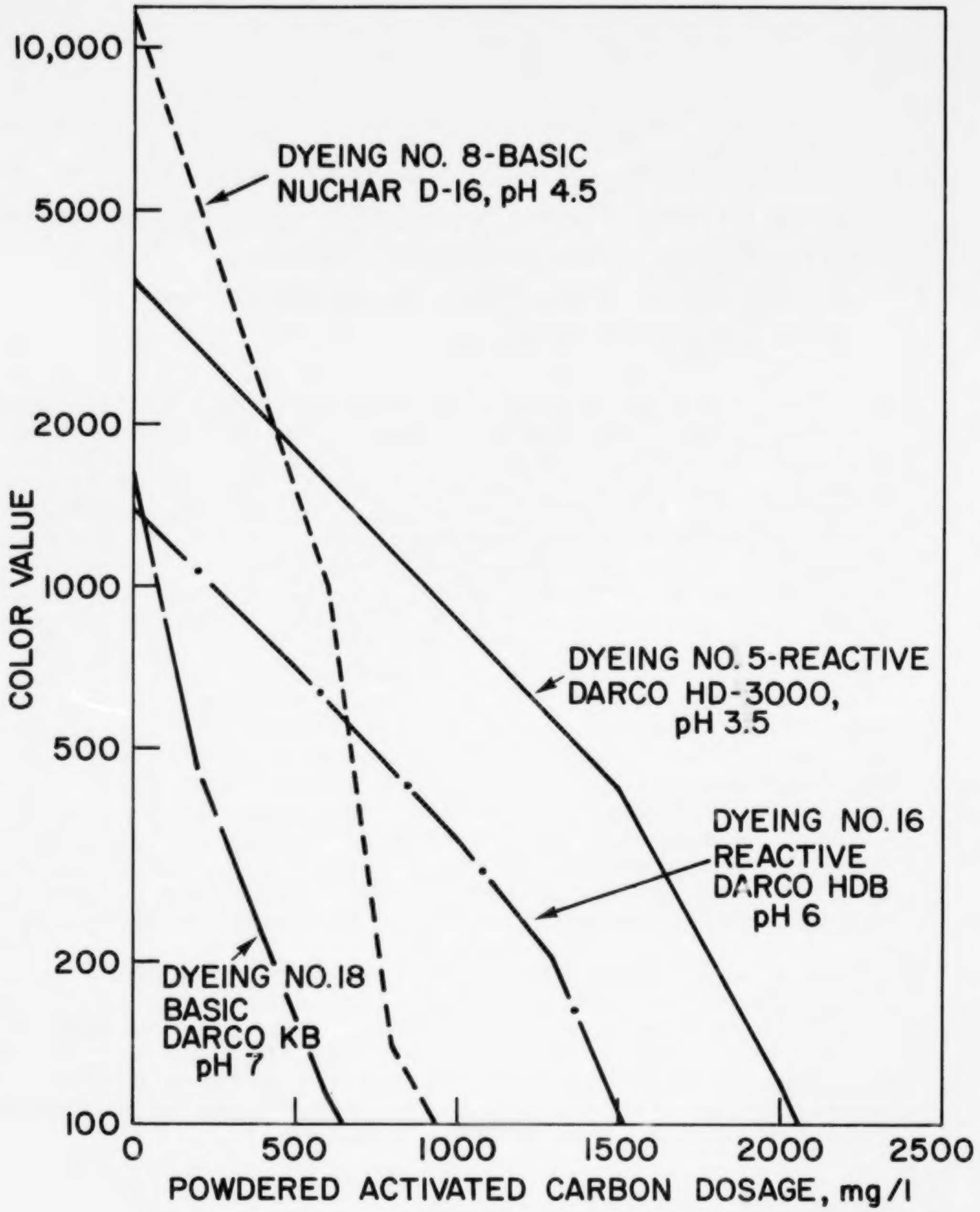

FIGURE 86. Comparison of Reactive and Basic Dyeing Wastewaters with Respect to Decolorization by Powdered Activated Carbon

$$(C_o-C)/m = KQ°C/(1+KC)$$

where

C_o = initial color (dye concentration)
C = residual (equilibrium) color (dye concentration)
m = weight of the adsorbent (carbon)
K = measure of the strength of adsorption
$Q°$ = adsorptive capacity

Figure 87 is a Langmuirian plot of the data for the reactive and basic dyeing wastewaters under the best conditions (pH and type of carbon) of treatment. While it may not be appropriate to generalize from the limited results of this study in which only two reactive dyeing wastewaters and two basic dyeing wastewaters were investigated, Figure 87 does suggest that basic dyes are more readily adsorbed by activated carbon than are reactive dyes. Similar calculations for wastes 10 (acid dye) and 20 (azoic dye) indicate a similar degree of adsorption for both, and of the same degree as for the basic dyeing wastewater no. 18. An attempt was made to linearize the adsorption data to fit a simple Langmuirian or Freundlich adsorption model, but the linear fit was not satisfactory for all the wastes. (Actually, there is no reason to expect a satisfactory fit to either model since "ADMI color" is a collective parameter expressing the response to several colored components, each with a different affinity for the carbon. The presence of other organics in the waste which compete with the dye molecules for the carbon surface is another factor negating a simple mathematical formulation.)

Table 73 also shows the TOC removals corresponding to the PAC doses which give the most efficient decolorization. The percent removals were quite variable, even for the same dye class (e.g., reactive or basic), ranging from 18% to 87%; only two of the wastes had removals greater than 50%. It is apparent that the dye molecules were selectively adsorbed relative to the other organic components.

Ozonation (Chemical Oxidation)

In order to ascertain which dyeing wastewaters, of those investigated, were most effectively decolorized by ozone and to compare the various dye classes as to their susceptibility to decolorization by ozone, Figures 88 and 89 were constructed. For each of the wastes, the results plotted are those

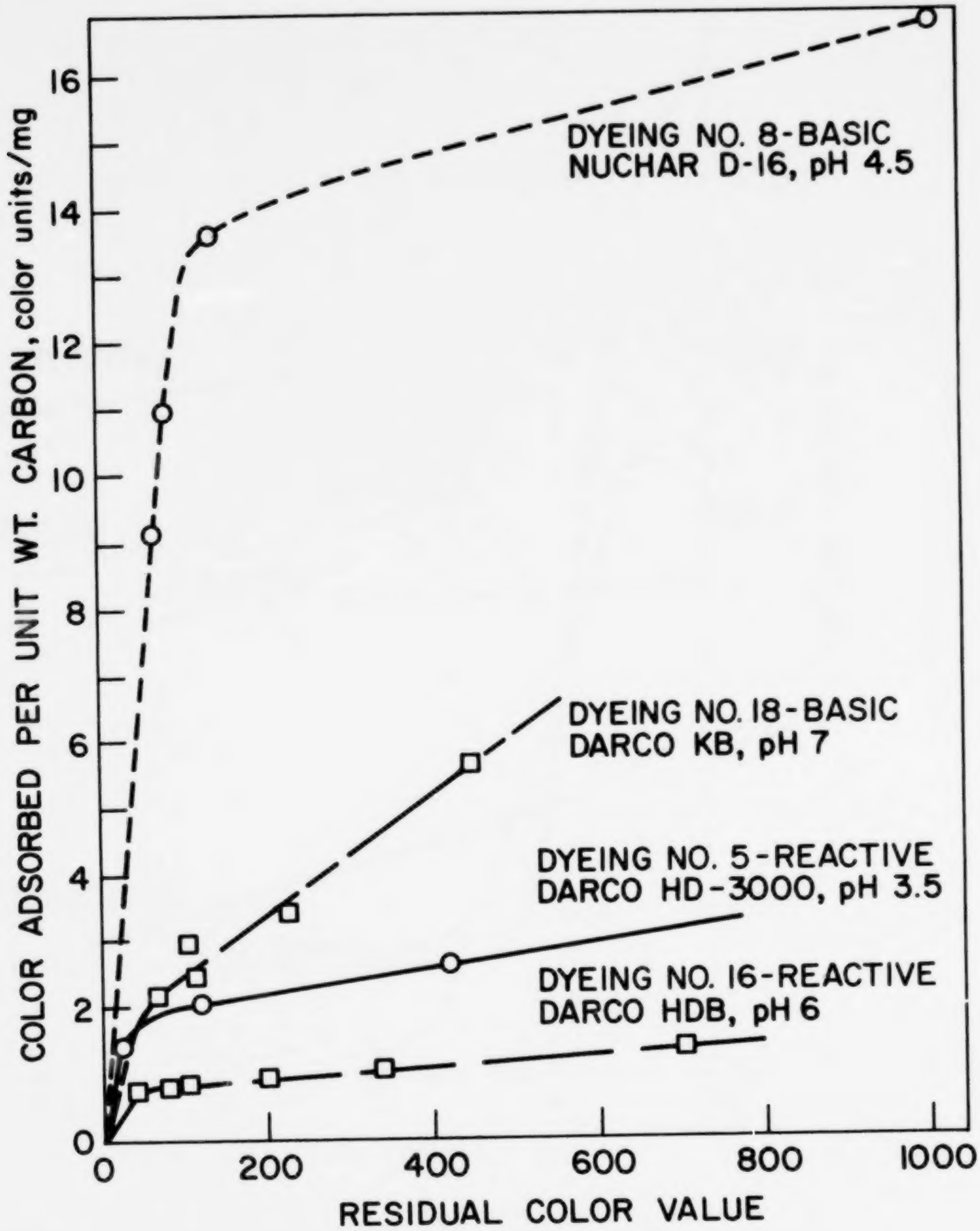

FIGURE 87. Adsorption of Color from Reactive and Basic Dyeing Wastewaters in Accordance with Langmuir Adsorption Model

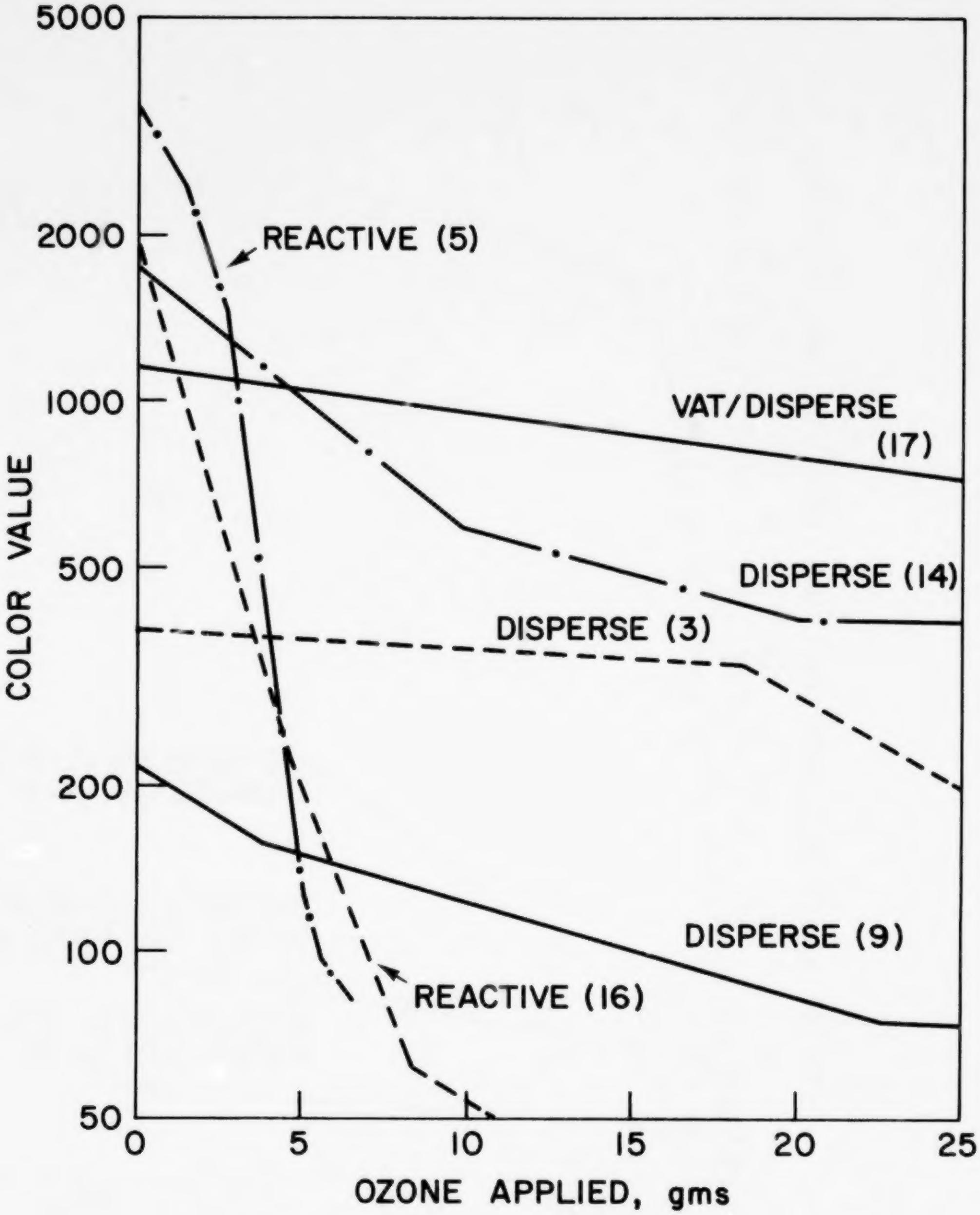

FIGURE 88. Comparison of Reactive and Disperse Dyeing Wastewaters with Respect to Decolorization by Ozone

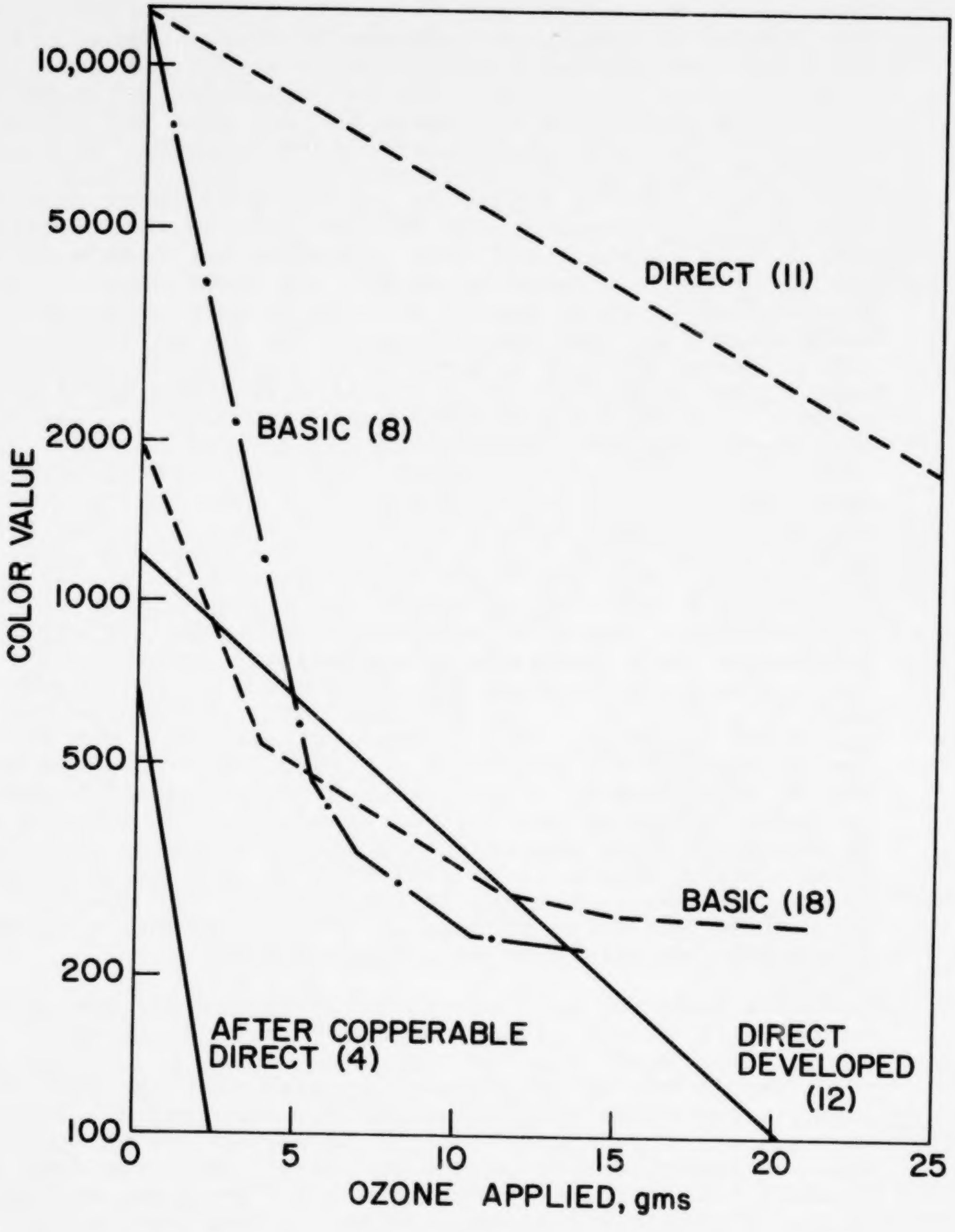

FIGURE 89. Comparison of Direct and Basic Dyeing Wastewaters with Respect to Decolorization by Ozone

obtained for a 7 scfh flow rate (which generally yielded about 5% O_3 by volume) and those pH conditions giving the best degree of treatment. Figure 88 clearly shows that the reactive dyes (wastes 5 and 16) were very efficiently decolorized by ozone, with 5 to 7 gms O_3 (approximately 1 gm/l) sufficient to decolorize the waste to less than 100 (95-97% reduction in color). The disperse dyes, however, as a class, were relatively poorly decolorized by ozone (wastes 3, 9, 14, and 17) as shown in Figure 88. Figure 89 shows that the basic dyeing wastewaters (8 and 18) were quite effectively decolorized by ozone but that ozonation was unable to decrease the color below a residual of 200-300 color units. The direct dyes varied in their susceptability to decolorization by ozone depending upon the nature of the direct dyeing application. Ozone was very efficient in treating the after-copperable direct waste (no. 4) and also relatively efficient in treating the direct-developed waste (no. 12); it was not very effective, however, in decolorizing the Direct Black 38 waste (no. 11). This could be due to the high initial color of waste no. 11 which required a greater quantity of ozone than the less-intensely colored wastes (compare the slopes for wastes 11 and 12 in Figure 89). It is apparent from Figure 89, however, that the basic dyeing wastewater no. 8, with the same initial color value as no. 11, was much more reactive toward ozone. Table 74 summarizes the effectiveness of ozone in decolorizing those dyeing wastewaters investigated. The basic dyeing wastewaters are categorized as moderately treatable only because of the residual color which appeared to be resistant to ozone. The classifications noted for the other dyeing wastewaters which are not shown in Figures 88 and 89 can be confirmed by comparing their decolorization responses to ozone, given by the figures in Section VII and the summary in Table 66, with the responses of the disperse and reactive dyes. Again, while it is difficult to generalize based upon a limited amount of data, it appears that the reactive dyes as a class are quite responsive to decolorization by ozone while the disperse dyes as a class are not.

Ozone is known to be a strong oxidant, but for the dyeing wastewaters investigated, the concentrations of total organic carbon were unaffected by ozone (see summary in Table 66). This should not be interpreted to mean that the specific organic compounds comprising the TOC were not oxidized by ozone since TOC is a collective parameter for all organic species regardless of oxidation state. What the data do mean, however, is that any oxidation which took place was not complete in converting organic carbon to inorganic carbon dioxide. Although the chemical oxygen demand (COD) of the wastes before and after ozonation was not measured, it might be hypothesized that the COD decreased as a result of the

TABLE 74. SUMMARY: DECOLORIZATION BY OZONE

Very treatable by ozone	Poorly treatable by ozone	Moderately treatable by ozone
Reactive dyeings - 5, 16	Disperse dyeings - 3, 9, 14, 17	Basic dyeings - 8, 18
1:2 metal complex dyeing - 2	Acid dyeing - 10	Sulfur dyeing - 15
After-copperable direct dyeing - 4	Direct dyeing - 11	Azoic dyeing - 20
Direct developed dyeing - 12		Disperse/acid/basic dyeing - 19
Disperse/acid/basic dyeing - 13		

Note: Dyeing wastewaters 1, 6, and 7 were not treated by ozone.

partial oxidation by ozone of the organic compounds comprising the TOC. The fact that the BOD of some of the wastes increased as a result of ozonation suggests that the organics were altered in part by ozone, being converted from non-biodegradable organics to organic compounds which were biologically oxidizable. Ozone has been demonstrated by several researchers to have this effect on organic wastes and one group[5] has even proposed ozone as a pre-treatment step for dyeing wastewaters prior to biological treatment.

The results in Section VIII suggest that the efficiency of ozone in decolorizing the various dyeing wastewaters is largely a function of the gas transfer characteristics of the reactor system. While no attempt was made to optimize gas transfer, the data confirm that increased partial pressures of ozone in the feed gas stream significantly increase the driving force for ozone dissolution and subsequent reactivity with the dye molecules. Better mixing in the reactor and a greater contact opportunity between the injected gas and the solution can result in a more efficient utilization of ozone and can decrease the quantity of ozone required to achieve a desired degree of decolorization.

It was also observed that, in general, acidic pH values (with the exception of wastewater no. 5) provided more effective decolorization of the wastes by ozone.

COMBINED BIOLOGICAL/PHYSICAL-CHEMICAL TREATMENT

Since the biological systems were generally very effective in reducing the BOD and TOC of the dyeing wastewaters but rather ineffective in decolorizing the wastes, and the physical-chemical treatment systems effectively decolorized the wastes but generally provided poor TOC and BOD removal, three dyeing wastewaters were investigated by coupling biological degradation with physical-chemical decolorization. Following 21 days of biological incubation as described in Section VI, the samples were filtered to remove the microorganisms and the resulting liquid was analyzed for TOC, BOD, and ADMI color. The 100% samples (i.e., full-strength dyeing wastewaters, undiluted) which had been seeded with acclimated sludge were then treated by either alum coagulation or powdered activated carbon adsorption under the appropriate dosage conditions which had proven to be most effective in the separate physical-chemical treatability studies. The results are shown in Table 75. Columns 2 and 3 in the Table should be identical, barring some small changes during storage between treatments. The combined treatment produced an effluent with greater than 85% removal of BOD, greater than 70% removal of TOC, and a residual color of less than 100 (with the exception of no. 18 which could have been decolorized further by a higher dosage of carbon as was shown in Figure 77).

These coupled treatability analyses suggest that the colored effluent from biological treatment systems can be subsequently decolorized by coagulation, carbon adsorption, or ozonation. Alternatively, if the dyeing wastewaters can be segregated in the plant, they can be decolorized by one of these physical-chemical treatment methods and then combined with the remainder of the organic wastewaters in the plant and treated biologically for BOD and TOC removal.

CONCLUSIONS

1. Dyeing wastewaters can be effectively treated with respect to BOD, TOC, and color removal if they can be segregated in-plant.

2. No one specific type of treatment will suffice for all dyeing wastewaters; the most effective type of treatment depends upon the type of dyeing performed and the chemical composition of the dye bath.

TABLE 75. RESULTS OF COMBINED BIOLOGICAL/PHYSICAL-CHEMICAL TREATMENT

Dyeing Wastewater No. 17 - Vat and Disperse Dyes on Polyester/Cotton

	Initial	After biol. treat.	Before phys. chem. treat.	After phys. chem. treat.[a]
ADMI color	365	313	296	68
Apparent color	1100	---	364	72
BOD_5, mg/l	360	38	---	--
TOC, mg/l	350	83	---	--

[a] 55 mg/l Al with no pH adjustment. Final pH 5.9.

Dyeing Wastewater No. 18 - Basic Dyes on Polyester

	Initial	After biol. treat.	Before phys. chem. treat.	After phys. chem. treat.[b]
ADMI color	1300	668	579	87
Apparent color	2040	---	1744	208
BOD_5, mg/l	1470	216	----	---
TOC, mg/l	1120	275	----	---

[b] 400 mg/l Nuchar D-16 at pH 6.7.

Dyeing Wastewater No. 20 - Azoic Dye on Cotton

	Initial	After biol. treat.	Before phys. chem. treat.	After phys. chem. treat.[c]
ADMI color	2415	1987	1683	18
BOD_5, mg/l	200	<1	----	--
TOC, mg/l	170	55	----	--

[c] 800 mg/l HD-3000 at pH 6.0

3. Disperse, vat, and sulfur dyeing wastewaters can be readily decolorized by coagulation with alum, but are not readily decolorized by activated carbon.

4. Reactive, basic, acid, and azoic dyeing wastewaters can be readily decolorized by activated carbon; basic dyes are more strongly adsorbed on carbon than reactive dyes.

5. Reactive dyes can be decolorized most effectively by ozone; disperse dyes are decolorized least by ozone.

6. BOD and TOC removal by physical-chemical treatment techniques, i.e., coagulation, carbon adsorption, and ozonation, is not very effective.

7. The organic constituents of the dyeing wastewaters are relatively biodegradable and BOD and TOC can be effectively reduced by biological treatment.

8. BOD removal is, generally, not inhibited by the dye molecules or other components of the dye bath.

9. Color, in general, is not readily removed by biological waste treatment, suggesting that the dye molecules are not readily biodegradable.

10. Nitrification fails to occur in some dyeing wastewaters. This is probably due to (1) presence of organic nitrogen compounds which resist ammonification and/or (2) inhibition of nitrification by some component(s) of the wastewater. The causative agents of the inhibitory action have not been identified.

11. Dyeing wastewaters can be effectively treated with respect to BOD, TOC and color removal by coupling biological treatment with physical-chemical treatment methods, the former to remove BOD and TOC and the latter for decolorization.

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SECTION IX
TEXTILE MILL EFFLUENT SURVEY

There is a paucity of data in the literature on contributions of dyes to trace metal concentrations in textile mill effluents. A paper presented by ADMI[1] calculated theoretically trace metal concentration for a class of dyes, depth of dyeing, dye bath liquor ratio, degree of dye exhaust, and water usage for a given application. Recently, Netzer, Miyameto, and Wilkinson[2] have determined concentrations of selected heavy metals in exhausted dye batch effluents. However, the range of dyes and applications covered in their report is very limited, specifically to rabbit fur dyeing, and dyeing of acrylic and nylon fibers.

It was, therefore, decided to undertake an analytical survey of dye batch wastes from textile mills for cadmium, chromium, copper, lead, mercury, and zinc. In view of the general concern whether benzidine is present in significant amounts in textile wastes, benzidine was included in the analytical survey. It must be emphasized that the samples analyzed were untreated samples from exhausted dye baths without any dilution from other textile operations such as scouring, rinsing, etc.

A discussion of the procedures used for the heavy metals is found in Appendix A and for benzidine in Appendix B.

SAMPLING PLAN

Samples of exhausted dye bath liquors along with plant service water sample were collected from textile mills by American Textile Manufacturers Institute (ATMI). Textile mills were selected for parcipitation in this program so as to represent a broad cross-section of the industry and to represent the more important types of textile manufacturers.

All samples were collected, preserved, and handled according to EPA methods[3] for extractable metals. Pyrex glass bottles of 200 ml capacity with lined plastic caps were used for sample collection. The small bottle was chosen to minimize breakage in shipment.

Samples for benzidine analysis were also collected in 200 ml Pyrex glass bottles and preserved by addition of 25 ml of concentrated HCl/liter of sample. Only exhausted dye bath samples were collected. Service water samples were not analyzed for benzidine.

RESULTS

Efforts were made to analyze the samples 14 days after the date of sampling to minimize variations in reported values due to shelf time.

For the purpose of interpretation of data, samples have been grouped by different dyeing systems depending upon the fabric or yarn dyed and the type of dye(s) used. Methods of application had no significant effect on pollutant concentrations in exhausted dye batch effluents and hence, were not considered as bases for dyeing systems. A total of 22 dyeing systems were thus established.

Following approximations have been used in computing the delta values between make-up water samples and effluent samples. Delta value for a given parameter of a sample is defined as $C_{sample} - C_{make-up}$, where C_{sample} and $C_{make-up}$ stand for the concentrations of the parameter in effluent sample and in make-up water respectively.

A. All process water values reported as less than detection limit are considered as zero values.

B. All effluent sample values reported as less than detection limits are considered to be equal to detection limit concentration.

C. In those cases where, for a given sample and trace metal, make-up water has a higher value than corresponding effluent sample, the value of effluent sample is taken into consideration.

D. If maximum value for a dyeing system is reported as less than detection limit, it is taken as being equal to detection limit.

E. All minimum values are reported as true values including those reported as less than detection limit.

Above approximations have been used in order to bias the values to the higher side, thus giving a worst possible case situation.

Results have been segregated by the parameter analyzed and tabulated. Tables 75 through 81 list by parameters the average values, maximum values, minimum values for each system, average values for all systems and the total number of samples analyzed.

DISCUSSION OF RESULTS

Cadmium

Out of a total of 21 dyeing systems surveyed, exhausted dye baths from 16 systems were found to contain an average 0.05 mg/l or less of cadmium, dye batch effluent from four systems contained on an average between 0.16 mg/l to 0.21 mg/l of cadmium and one system gave effluents containing 7.50 mg/l average cadmium. The five systems yielding dye bath effluents higher in cadmium concentrations are Cotton - Direct; Cotton - Direct, after copperable; Cotton - Fiber reactive; Viscose - Direct; and Wool - Acid premetallized. It appears that Direct dyes contain relatively higher amounts of cadmium than other classes of dyes.

Chromium

A total of 12 dyeing systems out of 21 systems analyzed were found to give dyeing wastes with an average of less than 0.1 mg/l of total chromium. Exhaust liquors from six systems contained average chromium values between 0.1 mg/l and 0.5 mg/l. Average chromium values ranging from 0.85 mg/l to 2.71 mg/l were observed in exhaust liquors from three systems. These three systems are Polyamide - Acid premetallized; Polyester, Wood - Disperse, Acid premetallized; and Viscose - Direct. It should be noted that many of the acid premetallized dyes contain chromium as a complex with dye molecules rather than as free metal.

Copper

As results in Table 77 indicate, copper was found in average concentrations of less than 0.1 mg/l in exhausted dye baths from 10 dyeing systems. Average concentrations between 0.1 mg/l and 1.0 mg/l were observed in exhaust liquors from five systems and average concentrations greater than 1.0 mg/l up to 12.05 mg/l were found in exhaust liquors of six systems. These six systems are Cotton - Developed; Cotton - Direct; Cotton - Direct, after copperable; Cotton, Polyester - Direct, Disperse; Polyamide - Acid; and Viscose - Direct. Many of the direct dyes are derivatives of copper -phthalocyanine which contains copper as a covalently bound complex. Also, some of the direct dyes are developed on the substrate by a treatment with copper salts after dyeing. This explains the predictably high values for copper observed in effluents from dye baths containing direct, direct after copperable, and direct developed dyes.

Lead

This metal is primarily present in dyes as a metal contaminant originating from lead lined equipment used in manufacturing of dyes. This explains the results that exhaust liquors from only three systems contained lead in average concentrations of less than 0.1 mg/l, whereas lead was present in average concentrations between 0.1 mg/l and 1.0 mg/l in exhaust liquors from 17 systems. Only one system, Viscose - Direct, gave an exhaust liquor with average concentration of greater than 1.0 mg/l.

Mercury

Generally, mercury is present in dyes as a contaminant coming from many of the common chemicals, such as caustic soda, sulfuric acid, etc., used in the manufacture of dyes. Some of the intermediates used in dyes are manufactured using mercury salts as catalysts and such dyes may contain small amounts of mercury. Examination of Table 79 shows that dye bath effluents from 15 systems out of a total of 21 systems analyzed contained on an average less than 1 ug/l while six systems contained between 1 ug/l and 3 ug/l of mercury. These systems are Cotton - Direct; Cotton - Naphthol azoic; Cotton - Sulfur; Cotton - Vat; Polyamide - Acid premetallized; and Wool - Acid premetallized.

Zinc

Analytical survey of exhausted dye batch showed rather wide prevalence of zinc in average amounts greater than 1.0 mg/l, but less than 4.0 mg/l. It was also observed that zinc was present in similar concentrations in process water samples analyzed. Presence of zinc in process water as well as dye batch effluents can be traced back to widespread use of zinc phosphates as a corrosion inhibitor. Effluents from eight systems were found to contain zinc in average concentrations of less than or equal to 1.0 mg/l, while effluents from 13 systems ranged from 1.0 mg/l to 4.0 mg/l in average zinc concentrations.

It was observed for those systems based on dyeing of cotton that concentrations of zinc in dye batch effluents were lower than corresponding concentrations in process water samples.

Benzidine

A relatively small number of direct dyes are presently produced from benzidine. However, because of general concern for presence of benzidine in waste waters and receiving streams, it was included in the analytical survey of dye bath effluents. Of the 21 systems investigated, 14 systems had effluents with less than or equal to 10 ug/l of average concentration of benzidine. The remaining seven systems had an average concentration of between 10 ug/l and 20 ug/l benzidine in their effluents.

It should be pointed out that the analytical method for analysis of benzidine is a sensitive method capable of detecting a few ug/l in water samples. However, presence of any color in the samples causes considerable interference. This is especially true if the color is yellowish brown and is extractable in ethyl acetate, which is used as an extractant.

Table 76: SURVEY OF DYEING WASTES FROM TEXTILE MILLS

Cadmium

Dyeing System	No. Of Samples Analyzed	Average Value mg/l	Maximum Value mg/l	Minimum Value mg/l
1. Acid Dyeable Rayon-Acid	1	0.02	0.02	<0.02
2. Acrylic-Basic	18	0.03	0.08	<0.005
3. Cotton-Developed	3	0.02	0.03	0.01
4. Cotton-Direct	10	0.16	0.44	<0.005
5. Cotton-Direct, After Copperable	8	0.21	0.33	0.06
6. Cotton-Fiber Reactive	15	0.20	0.56	<0.02
7. Cotton-Naphthol Azoic	7	0.02	0.05	0.01
8. Cotton-Sulfur	13	0.01	0.30	<0.01
9. Cotton-Vat	16	0.05	0.20	<0.005
10. Cotton, Acetate, Rayon, Acid Dyeable Rayon-Direct, Disperse, Acid Premetallized	5	0.05	0.11	0.02
11. Cotton, Polyester-Direct, Acid	--	--	--	--
12. Cotton, Polyester-Direct, Disperse	11	0.05	0.13	0.00
13. Polyamide-Acid	22	0.02	0.10	0.00
14. Polyamide-Acid Premetallized	7	0.02	0.08	<0.01
15. Polyamide-Disperse	10	0.02	0.10	0.00
16. Polyester-Disperse	40	0.05	0.55	0.00
17. Polyester Cationic-Basic	7	0.05	0.10	0.01
18. Polyester, Wool-Disperse, Acid Premetallized	2	0.02	0.02	<0.02
19. Triacetate-Disperse	9	0.02	0.11	0.00
20. Viscose-Direct	3	0.18	0.40	0.07
21. Wool - Acid	9	0.04	0.1	0.01
22. Wood -Acid Premetallized	2	7.50	15.00	< 0.005

Total Number of Samples Analyzed: 218
Average of Average Value Column: 0.42 mg/l
Weighted Average for all Systems: .115 mg/l

Table 77: SURVEY OF DYEING WASTES FROM TEXTILE MILLS

Chromium

Dyeing System	No. Of Samples Analyzed	Average Value mg/l	Maximum Value mg/l	Minimum Value mg/l
1. Acid Dyeable Rayon-Acid	1	0.27	0.27	0.27
2. Acrylic-Basic	20	0.03	0.06	0.00
3. Cotton-Developed	3	0.04	0.06	0.01
4. Cotton-Direct	10	0.07	0.10	<0.005
5. Cotton-Direct, After Copperable	9	0.07	0.10	<0.05
6. Cotton-Fiber Reactive	14	0.12	0.75	<0.02
7. Cotton-Naphthol Azoic	8	0.05	0.13	0.01
8. Cotton-Sulfur	13	0.08	0.30	<0.02
9. Cotton-Vat	17	0.07	0.14	<0.005
10. Cotton, Acetate, Rayon, Acid Dyeable Rayon-Direct, Disperse, Acid Premetallized	5	0.26	0.75	0.02
11. Cotton, Polyester-Direct, Acid	--	--	--	--
12. Cotton, Polyester-Direct, Disperse	11	0.04	0.10	0.00
13. Polyamide-Acid	22	0.08	0.29	0.00
14. Polyamide-Acid Premetallized	7	0.85	3.78	<0.01
15. Polyamide-Disperse	9	0.03	0.09	0.00
16. Polyester-Disperse	41	0.10	1.70	0.00
17. Polyester Cationic-Basic	7	0.05	0.10	0.00
18. Polyester, Wool-Disperse, Acid Premetallized	2	1.03	2.00	<0.05
19. Triacetate-Disperse	9	0.14	0.98	0.00
20. Viscose-Direct	3	2.71	7.90	0.07
21. Wool - Acid	9	0.11	0.60	0.01
22. Wood -Acid Premetallized	2	0.21	0.32	<0.1

Total Number of Samples Analyzed: 222
Average of Average Value Column: 0.31 mg/l
Weighted Average for all Systems: .152 mg/l

Table 78: SURVEY OF DYEING WASTES FROM TEXTILE MILLS

Copper

Dyeing System	No. Of Samples Analyzed	Average Value mg/l	Maximum Value mg/l	Minimum Value mg/l
1. Acid Dyeable Rayon-Acid	1	0.05	0.05	<0.05
2. Acrylic-Basic	20	0.09	0.46	0.00
3. Cotton-Developed	3	3.93	6.38	2.66
4. Cotton-Direct	10	12.05	15.10	8.50
5. Cotton-Direct, After Copperable	9	11.61	26.00	1.70
6. Cotton-Fiber Reactive	14	0.23	1.10	<0.02
7. Cotton-Naphthol Azoic	8	0.06	0.13	0.01
8. Cotton-Sulfur	13	0.08	0.45	0.02
9. Cotton-Vat	17	0.37	0.90	<0.03
10. Cotton, Acetate, Rayon, Acid Dyeable Rayon-Direct, Disperse, Acid Premetallized	5	0.05	0.12	0.00
11. Cotton, Polyester-Direct, Acid	--	--	--	--
12. Cotton, Polyester-Direct, Disperse	11	1.83	4.00	0.22
13. Polyamide-Acid	22	1.43	14.10	0.00
14. Polyamide-Acid Premetallized	7	0.48	1.65	0.00
15. Polyamide-Disperse	9	0.04	0.13	0.00
16. Polyester-Disperse	41	0.16	0.78	0.00
17. Polyester Cationic-Basic	7	0.05	0.10	0.00
18. Polyester, Wool-Disperse, Acid Premetallized	2	0.40	0.60	0.20
19. Triacetate-Disperse	9	0.08	0.20	0.02
20. Viscose-Direct	3	8.52	12.40	1.01
21. Wool - Acid	9	0.07	0.20	0.00
22. Wood -Acid Premetallized	2	0.05	0.10	0.00

Total Number of Samples Analyzed: 222

Average of Average Value Column: 1.98 mg/l

Weighted Average for all Systems: 1.53 mg/l

Table 79 : SURVEY OF DYEING WASTES FROM TEXTILE MILLS

Lead

Dyeing System	No. Of Samples Analyzed	Average Value mg/l	Maximum Value mg/l	Minimum Value mg/l
1. Acid Dyeable Rayon-Acid	1	0.25	0.25	<0.25
2. Acrylic-Basic	20	0.12	0.33	0.00
3. Cotton-Developed	3	0.15	0.25	0.05
4. Cotton-Direct	10	0.42	0.80	0.04
5. Cotton-Direct, After Copperable	9	0.60	1.2	<0.025
6. Cotton-Fiber Reactive	14	0.54	1.2	0.02
7. Cotton-Naphthol Azoic	8	0.16	0.40	0.00
8. Cotton-Sulfur	13	0.28	1.0	<0.02
9. Cotton-Vat	17	0.42	1.32	0.02
10. Cotton, Acetate, Rayon, Acid Dyeable Rayon-Direct, Disperse, Acid Premetallized	5	0.10	0.18	0.05
11. Cotton, Polyester-Direct, Acid	--	--	--	--
12. Cotton, Polyester-Direct, Disperse	11	0.20	0.40	0.00
13. Polyamide-Acid	22	0.21	0.41	0.00
14. Polyamide-Acid Premetallized	7	0.12	0.25	0.01
15. Polyamide-Disperse	9	0.08	0.25	0.00
16. Polyester-Disperse	41	0.18	0.90	<0.01
17. Polyester Cationic-Basic	7	0.26	0.90	0.05
18. Polyester, Wool-Disperse, Acid Premetallized	2	0.27	0.33	<0.20
19. Triacetate-Disperse	9	0.15	0.37	<0.05
20. Viscose-Direct	3	1.95	3.99	0.85
21. Wool - Acid	9	0.22	0.90	0.02
22. Wood -Acid Premetallized	2	0.10	0.10	<0.1

Total Number of Samples Analyzed: 222
Average of Average Value Column: 0.32 mg/l
Weighted Average for all Systems: 0.27 mg/l

Table 80 : SURVEY OF DYEING WASTES FROM TEXTILE MILLS

Mercury

Dyeing System	No. Of Samples Analyzed	Average Value mg/l	Maximum Value mg/l	Minimum Value mg/l
1. Acid Dyeable Rayon-Acid	1	0.6	0.6	0.6
2. Acrylic-Basic	19	0.39	0.5	0.05
3. Cotton-Developed	3	0.5	0.5	<0.05
4. Cotton-Direct	9	1.39	9.3	<0.05
5. Cotton-Direct, After Copperable	9	0.79	1.90	0.11
6. Cotton-Fiber Reactive	12	0.62	1.50	<0.5
7. Cotton-Naphthol Azoic	7	1.12	3.33	0.20
8. Cotton-Sulfur	12	1.15	5.0	<0.05
9. Cotton-Vat	16	2.20	17.0	<0.08
10. Cotton, Acetate, Rayon, Acid Dyeable Rayon-Direct, Disperse, Acid Premetallized	4	0.31	0.50	<0.05
11. Cotton, Polyester-Direct, Acid	--	--	--	--
12. Cotton, Polyester-Direct, Disperse	11	0.79	3.96	0.00
13. Polyamide-Acid	19	0.38	1.00	<0.2
14. Polyamide-Acid Premetallized	6	1.23	5.2	<0.05
15. Polyamide-Disperse	7	0.27	0.5	0.00
16. Polyester-Disperse	40	0.99	13.3	<0.05
17. Polyester Cationic-Basic	7	0.43	1.0	<0.20
18. Polyester, Wool-Disperse, Acid Premetallized	2	0.5	0.5	<0.5
19. Triacetate-Disperse	9	0.58	2.00	<0.02
20. Viscose-Direct	2	0.50	0.50	0.50
21. Wool - Acid	8	0.48	1.0	<0.05
22. Wood -Acid Premetallized	2	1.53	3.0	<0.05

Total Number of Samples Analyzed: 205
Average of Average Value Column: 0.80 ug/l
Weighted Average for all Systems: 0.86 ug/l

Table 81 : SURVEY OF DYEING WASTES FROM TEXTILE MILLS

Zinc

Dyeing System	No. Of Samples Analyzed	Average Value mg/l	Maximum Value mg/l	Minimum Value mg/l
1. Acid Dyeable Rayon-Acid	1	1.41	1.41	1.41
2. Acrylic-Basic	20	1.06	8.67	0.00
3. Cotton-Developed	3	0.66	1.26	0.08
4. Cotton-Direct	10	0.87	1.0	0.48
5. Cotton-Direct, After Copperable	9	1.02	1.50	0.60
6. Cotton-Fiber Reactive	14	0.65	3.3	0.04
7. Cotton-Naphthol Azoic	8	2.02	3.3	0.2
8. Cotton-Sulfur	13	0.54	1.82	0.07
9. Cotton-Vat	17	0.83	2.20	0.05
10. Cotton, Acetate, Rayon, Acid Dyeable Rayon-Direct, Disperse, Acid Premetallized	5	1.04	2.60	0.20
11. Cotton, Polyester-Direct, Acid	--	--	--	--
12. Cotton, Polyester-Direct, Disperse	11	0.46	1.34	0.00
13. Polyamide-Acid	22	1.39	2.35	0.00
14. Polyamide-Acid Premetallized	7	1.78	2.40	0.40
15. Polyamide-Disperse	9	1.06	1.90	0.10
16. Polyester-Disperse	41	1.53	7.27	0.00
17. Polyester Cationic-Basic	7	0.46	1.50	0.00
18. Polyester, Wool-Disperse, Acid Premetallized	2	1.54	1.88	1.20
19. Triacetate-Disperse	9	1.00	2.10	0.01
20. Viscose-Direct	3	1.32	2.00	0.40
21. Wool - Acid	9	3.43	8.2	<0.5
22. Wood -Acid Premetallized	2	3.10	3.69	2.5

Total Number of Samples Analyzed: 222
Average of Average Value Column: 1.29 mg/l
Weighted Average for all Systems: 1.22 mg/l

Table 82 : SURVEY OF DYEING WASTES FROM TEXTILE MILLS

Benzidine

Dyeing System	No. Of Samples Analyzed	Average Value mg/l	Maximum Value mg/l	Minimum Value mg/l
1.Acid Dyeable Rayon-Acid	--	--	--	--
2.Acrylic-Basic	23	10	10	< 1
3.Cotton-Developed	1	16	16	16
4.Cotton-Direct	10	13.4	44	<10
5.Cotton-Direct, After Copperable	12	16	44	<10
6.Cotton-Fiber Reactive	18	10	10	<10
7.Cotton-Naphthol Azoic	9	9.1	10.0	< 2
8.Cotton-Sulfur	11	15	50	<10
9.Cotton-Vat	12	9	18	< 1
10.Cotton,Acetate, Rayon,Acid Dyeable Rayon-Direct,Disperse,Acid Premetallized	5	6	10	1
11.Cotton,Polyester-Direct, Acid	2	10	10	<10
12.Cotton,Polyester-Direct,Disperse	19	7	10	1
13.Polyamide-Acid	24	11	20	<10
14.Polyamide-Acid Premetallized	5	14	20	<10
15.Polyamide-Disperse	9	4	10	< 1
16.Polyester-Disperse	49	14	60	< 1
17.Polyester Cationic-Basic	9	9	10	< 1
18.Polyester,Wool-Disperse,Acid Premetallized	3	1.67	3	< 1
19.Triacetate-Disperse	9	9.11	20	< 1
20.Viscose-Direct	2	10	10	10
21.Wool - Acid	9	3.78	20	< 1
22.Wood -Acid Premetallized	2	10	10	<10

Total Number of Samples Analyzed: 243
Average of Average Value Column: 11.5 ug/l
Weighted Average for all Systems: 11.8 ug/l

CONCLUSIONS

In this survey of waste waters from textile dyeing operations, approximately 220 samples of exhausted dye bath effluents, representing a total of 22 dyeing systems were analyzed under carefully controlled conditions for cadmium, chromium, copper, lead, mercury, zinc, and benzidine. Results obtained show that while some of the metals are present in significant quantities in exhausted dye bath liquors, especially when these metals are an integral part of dye molecule, generally dyes do not contribute significant amounts of metals or benzidine to dye baths. It should be emphasized that the effluent samples analyzed were untreated and undiluted samples. In a normal textile mill operation, these samples would be diluted by other operations such as scouring by a factor of 100 to 1,000. Further, these effluents will be treated in a waste water treatment plant when substantial removal of the trace metals and benzidine would occur. Typically, treated effluent from a textile mill would contain these trace metals and benzidine as contributions from dyes in amounts that are 1,000 to 10,000 times smaller than the values observed in this analytical survey.

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SECTION X

COMPENDIUM

INTRODUCTION

At some point in the manufacture of most textile products, whether for apparel, home furnishings, automotive fabric or other use, a chemical or "wet" processing stage is necessary to properly purify, color or finish the product to adapt it for its intended purpose. Such chemical treatment can result in the production of waste arising not only from the removal of natural or added impurities from the fiber but as residue of scouring and bleaching agents, dyes, chemical products used as "finishes", and auxiliary chemicals included to facilitate the particular process involved. Proper technology will minimize the production of waste from dyes and chemicals.

This survey will provide an overview of textile dyeing processes together with a description of dyes and chemicals used in commercial practice. These dyes and chemicals, any decomposition substances, and contaminants removed from the textile during dyeing are the chemical contributors to the water-pollution problem which the dyehouse will have to control.

Textile fibers are of many chemical types and are wet processed in many physical forms. Both factors help to determine the specific chemical treatment which may be applied.

A. Chemical Categories of Fibers

The chemical categories into which fibers may be divided are as follows:

Chemical Category	Example
Cellulosics	Cotton, linen, regenerated cellulose rayon
Cellulose esters	Acetate, triacetate
Proteins	Wool, silk
Polyamides	Nylon, "Quiana"
Polyacrylics	"Acrilan", "Creslan", "Orlon"
Polyesters	"Dacron", "Fortrel", "Kodel"
Polyolefins	Polypropylene
Aramide	"Nomex"

Polyurethane	Spandex
Fluorocarbon	"Teflon"
Inorganic	Glass Fiber

It should also be noted that a number of the non-cellulosic fibers listed above may be chemically modified by the fiber manufacturer to render them dyeable with acid and/or cationic dyes.

B. Physical Forms Processed

Textiles are dyed in the following physical forms:

Loose or Staple Fiber -

Discontinuous lengths of man-made fibers cut or broken into specified lengths from bundles or continuous filaments (tow). Natural fibers, e.g., cotton and wool, which have been subjected to no manufacturing processes, are in this category.

Tow -

Large bundles of nontwisted continuous monofilaments.

Top -

Combed and slightly twisted ropes of wool fiber or synthetic staple prior to being twisted and possibly plied to form staple yarn.

Yarn - Filament -

Continuous strands of, usually, multiple filaments. Some types are textured by the fiber producer or throwster, i.e., are mechanically treated to acquire twists, turns or crimp.

Staple -

Short lengths of natural and/or synthetic staple fibers mechanically twisted and spun into yarns. Filament and staple yarns may be dyed as skeins or as packages, i.e., wound on a perforated spindle or spring. This is usually the case where the fabric is to be woven or knit into a fancy or multicolored pattern. Where the warp (lengthwise) yarns of the fabric are to be all of a single color, the yarns may be dyed as a beam (wound essentially parallel to each other on a large perforated spindle or beam through which the dyebath is pumped), a rope warp (continuous bundle), or a flat warp (parallel); in the last case, the dyeing process is a continuous operation.

Fabric -

May be knit, woven, or nonwoven (interlaced fibers bonded into a sheet). Fabrics may be processed in the open width (under some tension), in rope form (relaxed, without tension), or, in the case of circular knit goods, in tubular form, i.e., unslit.

Garments -

Hosiery, sweater components. The physical form will determine to some extent whether a batch or a continuous operation will be used in wet processing. For example, yarn wound on tubes or cones, or individual units of apparel as hosiery, is not adapted to continuous handling whereas fabric, depending upon its construction, may be quite suited to this method.

Obviously, the physical form of the material to be processed and whether continuous or batch operation is to be used will in turn affect the design of the equipment in which the processing is to be carried out.

C. Machines for Dyeing

Dyeing machines may be divided into those used for batch processing (wherein each unit of the material to be dyed is subjected to the process over a substantial time period, often several hours), continuous processing (wherein an indefinite length of the material to be dyed is passed rapidly through the processing machinery so that the exposure at any given point in the material ordinarily does not exceed a few minutes) and semi-continuous, a combination of the two.

A very brief description of the basic types of equipment used for dyeing textiles is given below. Many variations are encountered. Open, closed and pressurized types are further options.

1. Batch Dyeing Equipment -

a. Jig - See Figure 90. This is a device for dyeing fabric in open width (flat) form in which cloth from a roll is drawn through heated dye liquor and rewound on another roll. This movement is continued back and forth until the dyeing is completed, the fabric being in constant motion. The liquor to goods ratio may be about four to one.

b. Beck - See Figure 91. In this machine a length of fabric in loose rope form, with ends sewn together to make a continuous loop is moved round and round constantly through the heated dyebath. Large becks can handle many parallel loops of cloth. A variation is a beck for open-width as opposed to roped fabric. The liquor to goods ratio may be as high as twenty to one.

c. Skein dyeing machine - See Figure 92. Machines of this type are designed to keep skeins of yarn in motion (rotating) while circulating dye liquor through them. Some machines simply keep the skeins moving in the liquor. Other types of skein dyeing equipment hold the skeins fixed on frames while circulating the dyebath with a pump or propeller.

d. Package machine - See Figures 93 and 94. A "package" for use on this machine is made by winding a single strand of yarn on a perforated tube or core. These packages are placed on perforated spindles in a closed vessel, and dye solution is forced through the package in alternating inside-out and outside-in directions by a suitable pump.

e. Beam dyeing machines - See Figure 95. For dyeing yarn in beam form several hundred parallel ends are wound on a large spool or beam with flanged ends. The beam is then processed much as if it were a single large package in a package dyeing machine. Some types of fabric may also be dyed by winding open width on a perforated beam and then circulating the dye bath through it. See Figure 96. The ratio of liquor to goods on package and beam dyeing machines may be seven or eight to one.

f. Hosiery dyeing machine - See Figure 97. One type of device for dyeing hosiery is the so-called paddle machine in which a rotating paddle wheel serves to keep the dyebath agitated and mesh bags containing the hosiery in constant motion. Another type consists of a horizontal perforated drum divided into several compartments with perforated walls. The drum is loaded with hosiery and is then rotated in the dyebath, reversing direction of rotation at intervals. The liquor to goods ratio is relatively high.

g. Jet dyeing machine - See Figure 98. This utilizes the same principle as a dye beck in that an endless loop of roped fabric is continuously conveyed in and out of the dye liquor. However in place of a rotating reel a powerful stream of the treating liquor producing a Venturi effect in guiding tubes is responsible for moving the fabric through the dyebath. The powerful jet of dye solution also provides excellent penetration and intimate

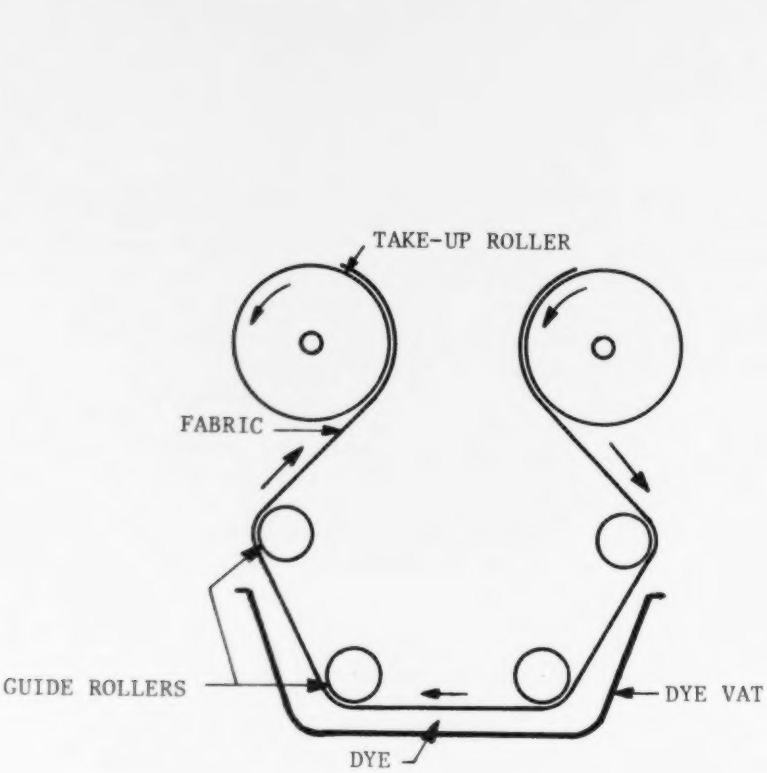
TAKE-UP ROLLER
FABRIC
GUIDE ROLLERS
DYE VAT
DYE

Figure 90. Dye Jig

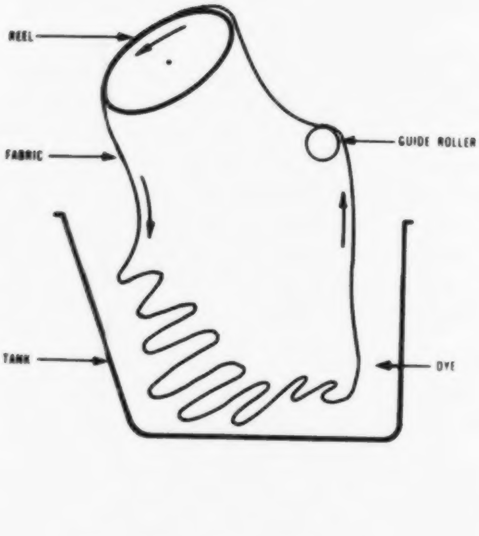
REEL
FABRIC
GUIDE ROLLER
TANK
DYE

Figure 91. Dye Beck

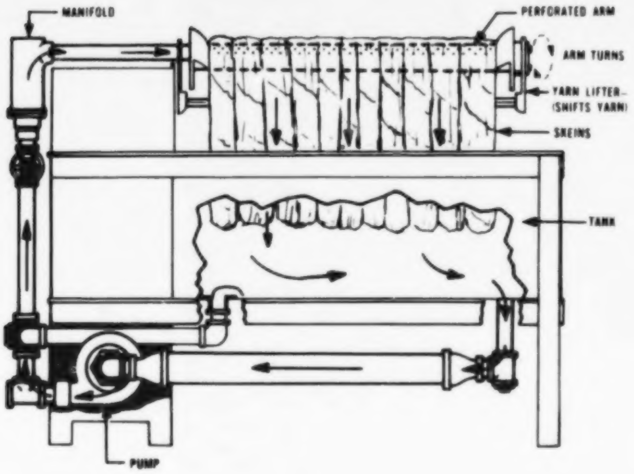
MANIFOLD
PERFORATED ARM
ARM TURNS
YARN LIFTER-
(SHIFTS YARN)
SKEINS
TANK
PUMP

Figure 92. Skein Dyeing Machine

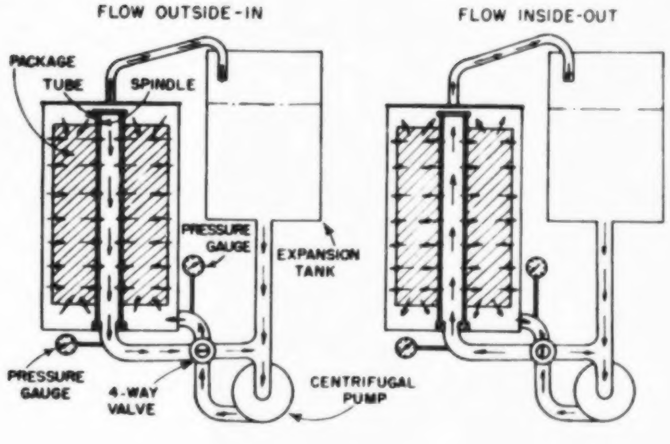
FLOW OUTSIDE-IN
FLOW INSIDE-OUT
PACKAGE
TUBE
SPINDLE
PRESSURE GAUGE
EXPANSION TANK
PRESSURE GAUGE
4-WAY VALVE
CENTRIFUGAL PUMP

Figure 93. Package Machine

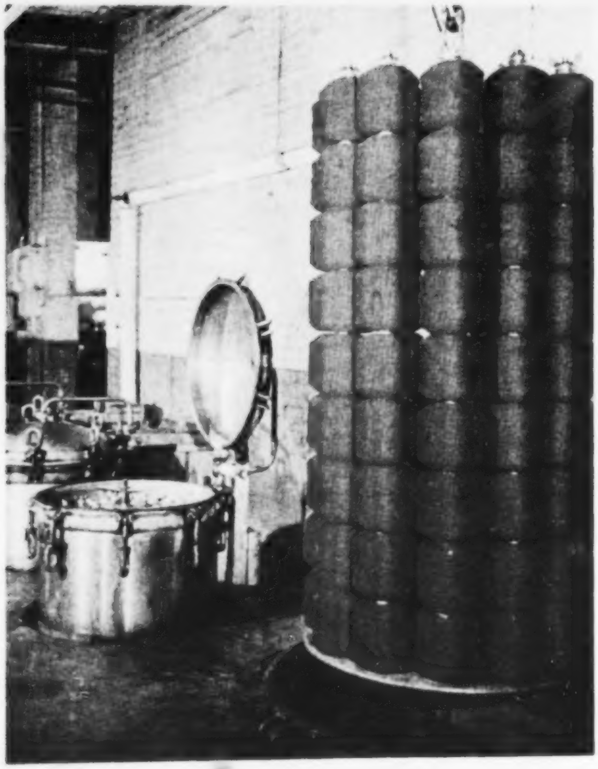

Figure 94

Package Dyeing

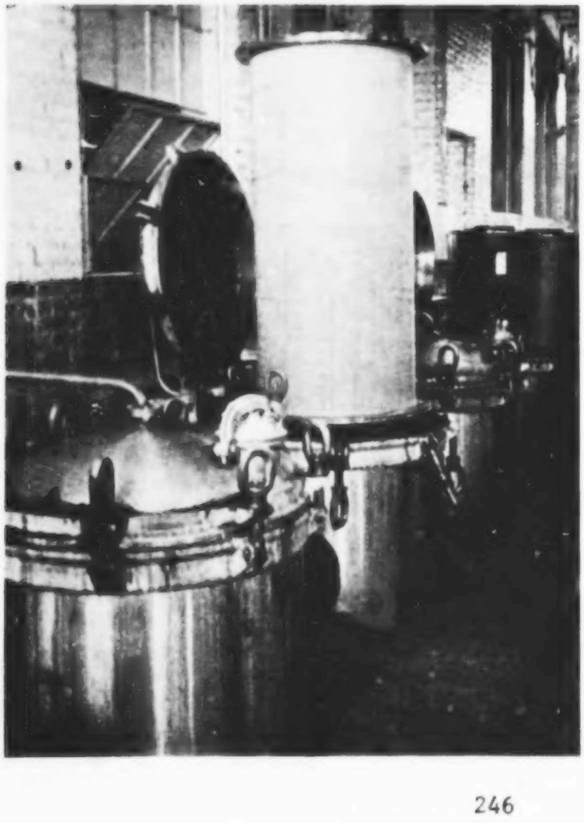

Figure 95

Beam Dyeing

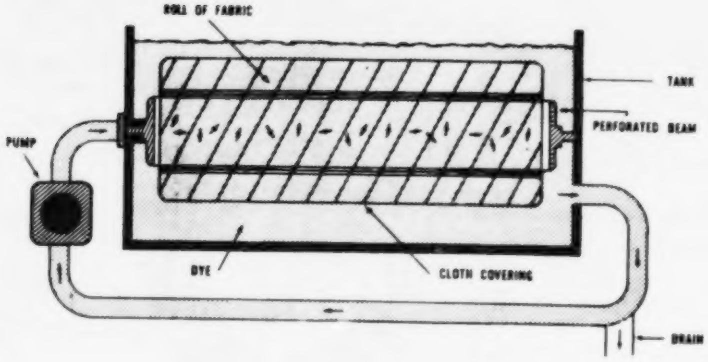
ROLL OF FABRIC
TANK
PERFORATED BEAM
PUMP
DYE
CLOTH COVERING
DRAIN

Figure 96. Beam Dyeing (Fabric)

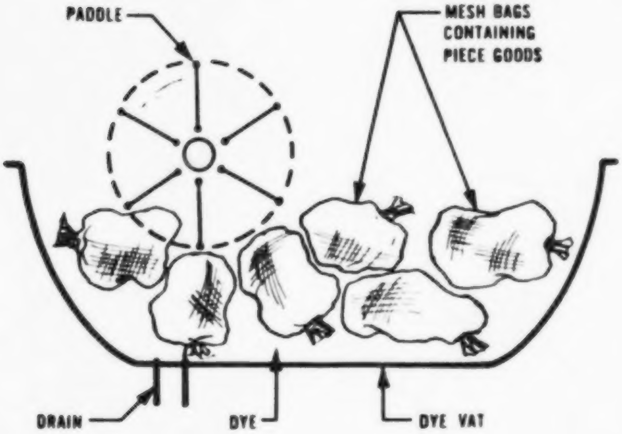
PADDLE
MESH BAGS CONTAINING PIECE GOODS
DRAIN
DYE
DYE VAT

Figure 97. Hosiery Dyeing

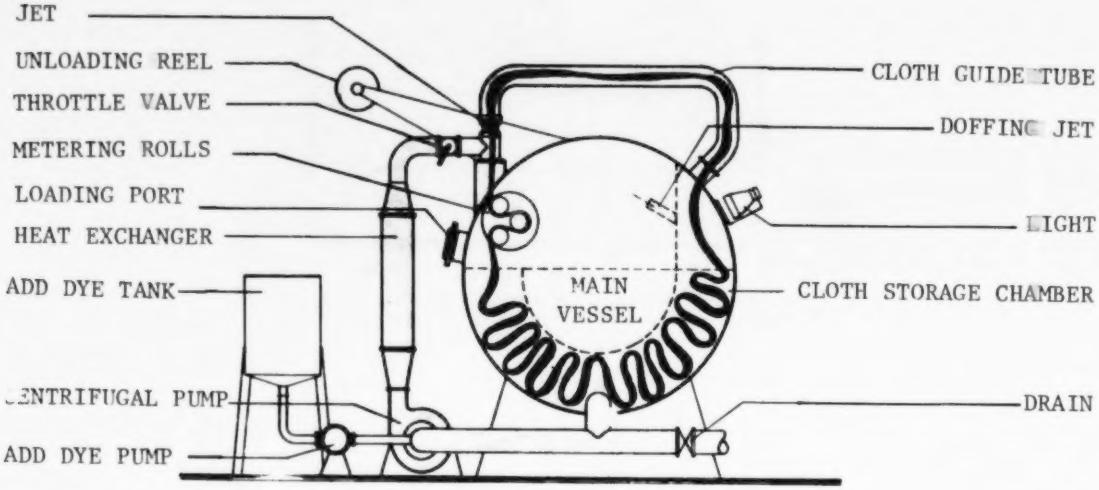
JET
UNLOADING REEL
THROTTLE VALVE
METERING ROLLS
LOADING PORT
HEAT EXCHANGER
ADD DYE TANK
CENTRIFUGAL PUMP
ADD DYE PUMP
CLOTH GUIDE TUBE
DOFFING JET
LIGHT
CLOTH STORAGE CHAMBER
DRAIN
MAIN VESSEL

Figure 98. Jet Dyeing Machine

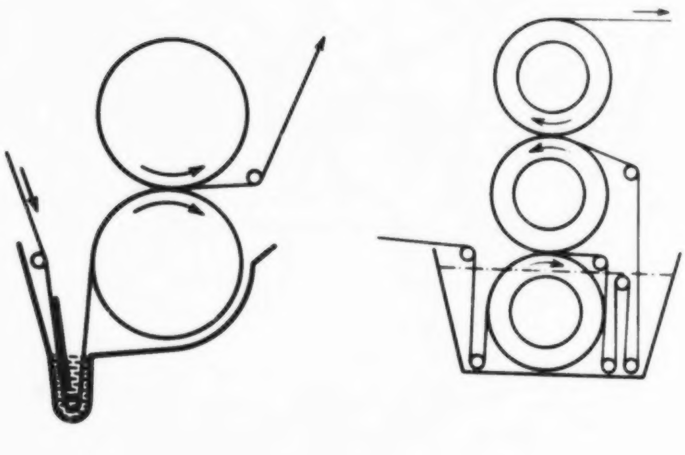

Figure 99. Padder (Two Types)

contact of dye and fiber, improving efficiency and uniformity.

2. Semi-Continuous Dyeing Equipment -

a. Pad-jig - The pad (see Figures 90 and 99), which is itself a device for continuous treatment of fabric, may be used in conjunction with other batch equipment or other continuous equipment. The pad is simply a device for rapidly impregnating fabric in open width form with any treating solution and then squeezing the fabric between rollers so that a controlled and uniform retention of treating solution is obtained. Initial saturation of cloth with dye solution on a padder followed by transfer to a jig (described above) for development of the shade over a period of time has proved very satisfactory for certain dyeings, hence the pad-jig system.

b. Pad-batch - In this system the fabric after impregnation and squeezing is simply rolled up on a beam ("batched") and allowed to stand for a period of time at room temperature. Slow rotation of the beam may be necessary.

c. Pad-roll - See Figure 100. Another system which provides an extended time for shade development following continuous padding is similar to the pad-batch just described except that provision is made for heating the padded fabric and storing it under controlled temperature and humidity conditions in a movable chamber.

3. Continuous Dyeing Equipment -

a. Pad-Steam Range - See Figure 101. This equipment was designed for the continuous dyeing of open-width fabric with vat dyes. The most popular arrangement is, as shown, first to apply an aqueous dispersion of unreduced vat dye (pigment), dry, pad in an alkaline sodium hydrosulfite solution, expose to air-free saturated steam for one minute or less, then oxidize, wash and dry. Cloth speeds of one hundred yards per minute or so are not uncommon.

b. Thermosol range - Sometimes described as a "thermo-fixation" unit, this range is based on the ability of polyester fiber to absorb certain dyestuffs uniformly (i.e., to dye) under the influence of dry heat. After being padded with a dispersion of a disperse dye the fabric is dried, then passed into the thermosol oven where it is exposed to heat in the range of 390° to 450° F for a period of 90 to 15 seconds after which the goods are washed and dried. The thermosol range and the pad-stream range (3,a above) are commonly combined to dye in one

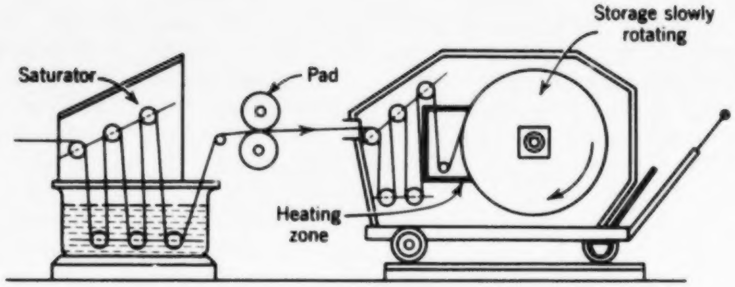
Storage slowly rotating
Saturator
Pad
Heating zone

Figure 100. Pad-roll Machine

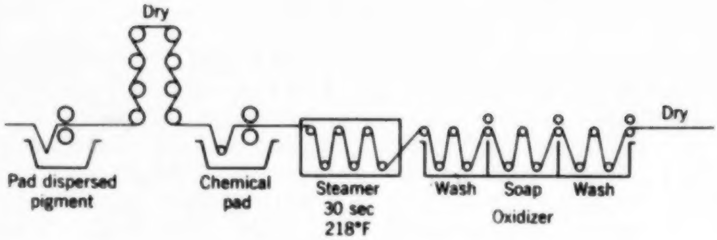
Dry
Dry
Pad dispersed pigment
Chemical pad
Steamer 30 sec 218°F
Wash
Soap
Wash
Oxidizer

Figure 101. Pad-steam Range

passage blended fabric comprised of polyester and cellulosic fibers. See Figure 102.

c. Carpet dyeing range - The difference in physical structure between carpets and other woven or knitted textiles requires a modified handling system for continuous dyeing. One such system is the Butterworth-Kusters range shown in Figure 103. The carpet is first wet out with chemicals (usually including a latent foaming agent), then the dye is metered to the surface of the carpet by a doctor blade arrangement which is furnished by a roll revolving in slightly thickened dye liquor. The carpet progresses to a loop steamer where it is festooned so that no contact is made with the carpet face. Dyeing takes place in the steamer, after which the carpet is washed free from excess dye and chemicals.

d. Indigo dyeing range for yarn - See Figure 104. Cotton yarn in the form of rope warps is dyed continuously with indigo in the sequence of operations shown. Each box or vat, usually holding 2,000 gallons or more is equipped with guide rollers and has squeeze rolls at the exit end. Between and above the dye vats, rollers are suspended for "skying" or air oxidation of the previously applied indigo solution which has been put into its reduced state by the addition of sodium hydrosulfite and sodium hydroxide. After the required number of reduced dye - air oxidation cycles a boiling water wash is usually given, then the warps are run over steam heated cylinders to dry them.

PREPARATION OF TEXTILES FOR DYEING

A. Impurities to be Removed

In order to be successfully dyed, printed, or otherwise finished, textile fibers must first be put into a reasonably pure state, that is, most of their natural impurities and any foreign matter accidentally or deliberately introduced in processing must be removed. The method by which this step is accomplished will depend upon the nature of the fiber.

Impurities associated with the various fibers are listed below.

Cotton

Motes - small pieces of foreign vegetable matter.

Spinning Oil - a hydrocarbon oil or other oily material applied as a lubricant

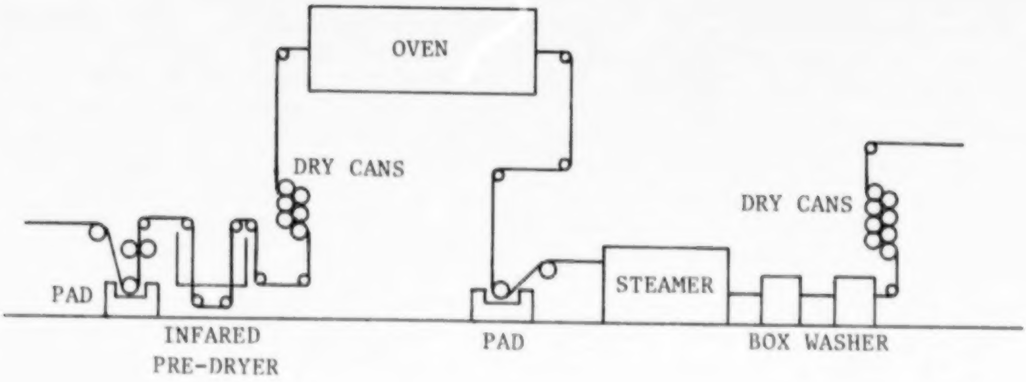
OVEN
DRY CANS
DRY CANS
PAD
STEAMER
INFARED
PRE-DRYER
PAD
BOX WASHER

Figure 102. Thermosol, Pad-steam Range

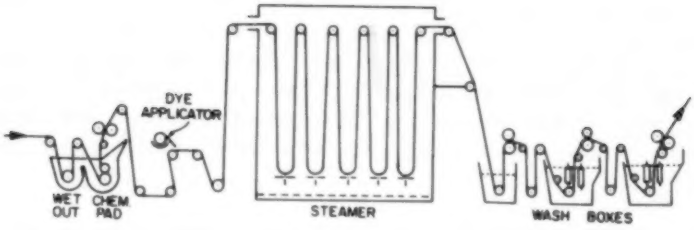
DYE
APPLICATOR
WET
OUT
CHEM.
PAD
STEAMER
WASH BOXES

Figure 103. Carpet Dyeing Range

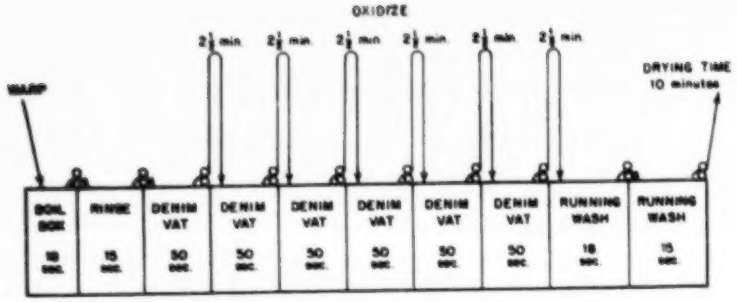
OXIDIZE
2½ min
2½ min
2½ min
2½ min
2½ min
2½ min
DRYING TIME
10 minutes
WARP
BOIL BOX
18 sec.
RINSE
15 sec.
DENIM VAT
50 sec.
DENIM VAT
50 sec.
DENIM VAT
50 sec.
DENIM VAT
50 sec.
DENIM VAT
50 sec.
DENIM VAT
50 sec.
RUNNING WASH
18 sec.
RUNNING WASH
15 sec.

Figure 104. Indigo Dyeing Range

to staple fibers to facilitate spinning.

Warp size - a glutinous solution, e.g., of starch, polyvinyl alcohol, or acrylic resin, applied to impart smoothness and strength to warp yarns to enable them to withstand mechanical abrasion during weaving.

Protein

Ash

Pectins

Wax

Pigment

Wool

Grease - a fatty wax coating the fiber surfaces.

Suint - dried perspiration of the sheep, rich in potassium salts.

Sand and dirt

Burrs and other vegetable matter

Spinning oil

Warp size

Synthetics

Finish applied by the fiber producer

Oily and carbonaceous matter from machines

Warp size

Spinning oil

Tint - a colorant applied by the producer or spinner to identify certain yarns.

B. Chemical Processes Applied to Textiles Before Dyeing

1. Desizing -

Desizing is a process in which starch-based warp size is hydrolyzed by acid or digested by enzymes to render it soluble in water and therefore readily removable by washing. Polyvinyl alcohol and acrylic sizes are usually removed directly in scouring.

2. Scouring -

Scouring consists of a hot alkaline treatment in which oily, waxy or greasy material or acquired impurities as well as some ash, pectins and protein, if present, are removed from fibers. The action can involve saponification and emulsification as well as simple solution of the impurities in the alkaline liquor. Scouring with chlorinated hydrocarbon solvents is also used to some extent.

3. Carbonizing -

Carbonizing is used to remove unwanted vegetable matter or fibers from wool in stock or fabric form. The action takes place by deliberately drying acid into the material under conditions which will decompose the vegetable materials to a friable powder ("carbon") which can be beaten out of the goods.

4. Bleaching -

Bleaching is used to destroy residual natural color in fibers remaining after the scouring process. It is an oxidation process usually effected with hydrogen peroxide or sodium hypochlorite.

5. Mercerizing -

Mercerizing is the treatment of cotton yarn or fabric, while under tension to prevent shrinkage, with sodium hydroxide solution in the concentration range of 16 to 25 percent. The goods are rinsed nearly free of alkali before the tension is released. The result is a cotton fiber which has a desirable subdued luster and substantially greater dyeability.

The equipment used for the above preparatory operations may be either of the batch or of the continuous variety; the latter predominates and in general consists of a sequence beginning with a pad for impregnation with chemicals followed by some type of conveying system in which the goods are carried through steaming or heating units while the chemicals act, then neutralizing and washing as necessary. In the case of fabric mercerizing, the cloth as it moves is held under tension until most of the sodium hydroxide solution is washed out.

Typical sequences in the preparation of the important fibers are as follows:

Cotton: Desizing, scouring, bleaching, mercerizing (optional)

Wool: Scouring, carbonizing, bleaching (optional)

Synthetics: Scouring, bleaching (optional)

DYEING

A. Definition

A dye can be loosely defined as a chemical compound which when properly applied to a substrate from solution or fine dispersion will color it with some degree of permanence. Normally the process is not merely a surface coloration but a cross-section of the substrate will be found to be uniformly penetrated and colored.

B. Classifications

There are in excess of 2,000 known dyes, some 1,400 being regular articles of commerce in the United States as indicated in PRODUCTS 75.*

The Colour Index+ divides all dyes into 22 more or less distinct chemical classes, some of the more important of these being for example azo, anthraquinone, stilbene, triarylmethane, azoic, and methine. Of greater value to the dyer is a classification based on usage or method of application. Included in this system are acid, direct, developed, mordant, metal complex, basic (or cationic), disperse, vat, soluble vat, sulfur, reactive, azoic (or naphthol), oxidation dyes, and pigments. The class names indicate to the dyer both the fibers to which each is applicable and the method by which it is applied.

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*A buyers guide to US producers and suppliers of dyes, pigments and chemical specialties for the textile wet processing industry published annually by the American Association of Textile Chemists & Colorists.

+ Third edition. 1971. Published jointly by the Society of Dyers and Colourists (England), and the American Association of Textile Chemists and Colorists (USA).

Table 83 will serve to relate the usage or application class of dyes to the fiber types upon which they may be applied; it also illustrates the overlapping and diversity of their chemical constitutions. Reference to the Colour Index under the "constitution numbers" shown usually will provide the exact chemical structure of a dyestuff.

C. Mechanisms; Principles

The mechanisms by which dyes are absorbed and retained by textile fibers are exceedingly complex.

In general, dyes in solution or in a finely dispersed state are preferentially absorbed by a fiber substrate in the dyebath. The forces responsible for the attraction and retention of the dye molecule by the fiber may be chemical (secondary valence forces, ionic charges, covalent bonds), or physical, or both. Such factors as time, temperature, pH and the presence of auxiliary chemicals (e.g. electrolytes, solvents, surface active agents) may affect the efficiency of a given dyeing process and the uniformity with which the dye is absorbed.

From a physical standpoint it is necessary that all surfaces of the material to be dyed be furnished continuously with dye solution. This can be done either by moving the material through the dye liquor or by forcing the dye liquor through the material. This is the basis on which machines for dyeing are designed. As for all wet processing, the dyeing machine must be adapted to the physical form of the goods.

To bring about dyeing in a reasonable length of time, the rate of diffusion of dye molecules into the substrate fiber is frequently accelerated by raising the dyebath temperature. Elevated temperatures also facilitate uniform distribution of dye throughout the material being dyed. In the case of the more hydrophobic synthetic fibers accelerated dyeing may be accomplished by (a) the use of organic substances known as carriers and/or (b) the use of closed dyeing systems allowing dyeing temperatures as high as 150°C.

Continuous dyeing methods may be used where the production volume is sufficient to provide economic justification and the mechanical structure of the material permits. These involve a series of steps commencing with the uniform impregnation of the material with the dye solution or dispersion under conditions which minimize substantive absorption. Subsequently, the material may be dried and then heated at elevated temperatures to effect diffusion

TABLE 83

CLASSIFICATION OF DYES* BY USAGE AND CHEMICAL NATURE

Chemical Class	Colour Index Constitution Numbers	Fiber Types															
		Cellulosic					Protein		Cellulose Esters	Polyamide			Polyester		Polyacrylic		
		Direct	Sulfur	Naphthol	Vat	Reactive	Acid	Mordant	Disperse	Acid	Disperse	Cationic**	Disperse	Cationic**	Acid	Disperse	Cationic
Azo	11000-36999	X				X	X	X	X	X	X	X	X	X	X	X	X
Stilbene	40000-40999	X				X											
Quinoline	47000-47999	X					X		X	X	X	X	X	X	X	X	X
Methine	48000-48999	X										X		X			X
Oxazine	51000-51999	X	X					X				X		X			X
Anthraquinone	58000-72999	X			X	X	X	X	X	X	X	X	X	X	X	X	X
Phthalocyanine	74000-74999	X	X	X	X	X	X			X		X		X	X		X
Acridine	46000-46999		X									X		X			X
Diphenylmethane	41000-41999																
Thiazole	49000-49399		X			X		X				X		X			X
Indamine, Indophenol	49400-49999																
Azine	50000-50999		X				X			X		X		X	X		X
Thiazine	52000-52999		X		X							X		X			X
Sulphur	53000-54999		X		X												
Azoic	37000-39999			X													
Indigoid	73000-73999				X		X			X					X		
Nitroso	10000-10299						X	X	X	X	X		X		X	X	
Nitro	10300-10999						X	X	X	X	X		X		X	X	
Triarylmethane	42000-44999						X	X		X		X		X	X		X
Xanthene	45000-45999						X	X		X		X		X	X		X
Indamine, indophenol	49400-49999	X					X		X	X	X	X	X	X	X	X	X

*Pigment colorants applicable to any fiber by a resin bonding process but chiefly used on cotton, are not included here.

Note: The classes of dyes listed under each fiber type represent the important usage. Infrequently, dyes not customarily employed on a given fiber may be used, possibly with special application methods. E.g., vats on wool, naphthols on polyester, cationics on cellulosics, etc.

** Applicable only to "cationic dyeable" fiber.

of the dye into the fiber, as in the thermosol process. In other cases as for example with vat and sulfur dyes, with or without drying the material is next impregnated with chemicals which will convert the dye to a substantive form, and then it is steamed to diffuse the substantive dye into the fiber; in a following unit a chemical treatment may be employed to insolubilize the absorbed dye within the fiber.

D. Properties of Dyes and Methods of Application

As can be noted in Table 83, different fibers can often be dyed with the same dye class. This table also shows that several chemical classes of dyes are often found in one usage or application class. Therefore, in the information given below, emphasis is primarily on the application class of dyes and its properties, with appropriate references to the fiber types for which the class may be used. The following information for the most part has been adapted from the preambles to the respective sections in the Colour Index.

1. Direct Dyes -

Direct dyes are used generally because of economics and ease of application. These dyes were originally designed and marketed for dyeing cotton and are defined as "Anionic dyes substantive to cellulose when applied from an aqueous bath containing an electrolyte." They color cellulosic materials from a neutral or slightly alkaline bath, at or near the boil, to which sodium chloride or sulphate is added in such quantities and at such intervals of time appropriate to the dyeing properties of individual dyes.

The majority of direct dyes belong to the Dis-, Tris- and Polyazo classes, the remainder being Monoazo, Stilbene, Oxazine, Thiazole, and Phthalocyanine compounds.

Some direct dyes have extensive use also on paper, leather, wool, silk, nylon, bast fibers and for many miscellaneous purposes.

Direct dyes may be processed or designed specifically for the following after-treatments (after the initial dyeing process) for improvement in fastness properties:

a. development on the fiber to a more complex dye through diazotising and coupling with a developer such as beta-napthol.

b. aftertreatment on the fiber with salts of metals, such as copper or chromium, to form metal complexes.

c. aftertreatment on the fiber with formaldehyde.

d. aftertreatment on the fiber with a cationic dye complexing agent.

2. Vat Dyes -

Vat dyes are used generally for their high fastness properties, particularly resistance to hypochlorite bleaching on cellulosic fibers.

These dyes, with very few exceptions, fall into two clearly defined groups, indigoid and anthraquinonoid. Included in the former are indigo, thioindigo and their derivatives while the latter include derivatives of anthraquinone as well as heterocyclic quinones. Characteristic of all these compounds is the ketonic group $>C=O$ which, on reduction, forms the leuco derivative $>C-OH$. As leuco compounds are capable of forming water-soluble alkali metal salts, the water-insoluble vat dyes may be brought into solution by reduction in alkaline liquor, in which form they exhibit affinity for textile fibers; subsequent oxidation reforms the insoluble dyestuff.

Vat dyes are available from manufacturers as finely divided water-insoluble pigments and as such they have no true affinity for fibers. They may be applied to fibers in the sodium leuco form, produced by first "vatting" the dye in the presence of sodium hydrosulfite and sodium hydroxide. The affinity of this reduced dye for fiber is so high however that it is often desirable in order to avoid non-uniform dyeing, to distribute the finely divided pigment form of the dye throughout the goods, then introduce the chemicals necessary to bring about reduction and consequent dyeing. After the dye has been absorbed by the fiber, it is reconverted to the insoluble pigment state within the fiber by oxidation with an agent such as hydrogen peroxide, then soaped and rinsed. The initial distribution of dye pigment can be by batchwise or by continuous methods. If the former, the rate of deposition (or "exhaustion") of the pigment onto the fiber surfaces from the aqueous dispersion may be controlled by the addition of electrolyte to the pigmentation bath.

Pre-pigmentation of loose fibers, yarn packages, knitgoods on the beck, and woven fabrics on the beam dyeing machine is a valuable aid to level dyeing in aqueous development processes.

In continuous applications the initial step is uniform impregnation on a padder with dispersed vat dye pigment. In fact the pigment-padding process is the basis for most continuous vat dyeing procedures, e.g., pad-steam. Here the pigmented cotton fabrics, preferably pre-dried, are passed through a cold padding liquor containing caustic soda and sodium hydrosulphite. Reduction and fixation are achieved by steaming at atmospheric pressure, e.g., 30 seconds at 100-105°C. This is followed by continuous oxidation and soaping treatments as part of the continuous sequence.

If the sodium leuco compounds are acidified, acid leuco compounds can be prepared. Such compounds possess even less affinity for the fiber than dispersed pigment and have been used to enable level dyeings to be obtained from dyes which possess so great an affinity that they are difficult to apply evenly by the normal process.

3. Sulfur Dyes -

Sulfur dyes are used in deep shades for economic reasons and fastness to washing. They are employed to produce a wide range of shades on cotton and rayon and to some extent on synthetic blends.

Sulfur dyes are made from organic compounds with nitro and amino groups by reactions with sulfur or sodium sulfide at high temperatures. Although sulfur dyes have been made and used for over 75 years, definite chemical structures have not been established for many of them.

The mechanism of dyeing is very similar to that of the vat dyes in that they are converted to the soluble leuco form by chemical reduction. Specifically, alkaline sodium sulfide is used for this purpose.

Sulfur dyes are commonly available in liquid form, pre-reduced, so that other than the liquid dye all that ordinarily need be added to the dyebath is electrolyte. If an unreduced form of the dyebath is purchased it is boiled with a strong solution of sodium sulfide together with sodium carbonate to reduce and dissolve it. Again, common salt or sodium sulfate is used as electrolyte in the batch dyeing process. After the dye has been absorbed by the fiber it must be converted back to the insoluble form by an oxidation step. Dye in the pre-reduced leuco stage may also be applied by a continuous system. A slight excess of sodium sulfide is normally present during application. The fabric is padded, steamed, or dryed and washed. Oxidation for either batch or continuous method is accomplished by treatment with sodium bichromate, hydrogen peroxide, sodium perborate or potassium iodate. A variation of the continuous process is to pad on unreduced pigment, dry, pad with sulfide, steam, oxidize and wash.

4. Azoic Coloring Matters -

These products are used primarily to produce bright shades, principally reds, with good washfastness and which in many cases are fast to bleaching.

The products referred to are those used to produce insoluble azo dyes (commonly called "naphthol" dyes in the trade) in situ on a textile substrate, usually cotton. The basic principle of their application is the introduction of two small soluble components into the fiber and the use of suitable conditions for coupling to occur, resulting in the production of one larger, insoluble colored molecule. One component is selected from the available Colour Index Azoic Coupling Components and the second from the Colour Index Azoic Diazo Components. The latter are diazotised primary amines, or the parent amines when the dyer caries out the diazotisation. The former are often known as naphthols because the majority are derivatives of B-naphthol, and some commercial products have been sold under this name.

The azoic coupling component is insoluble in water and must be converted to the soluble salt, e.g., the sodium salt, by means of caustic soda, usually with the aid of sulfonated oils, alcohol or Cellosolve. Formaldehyde may be added to stabilize this solution.

Azoic diazo components are marketed in two main forms: (1) as the free base, hydrochloride or sulphate of a primary amine which must be diazotised in the normal manner for such chemical compounds; (2) as stabilized diazo compounds generally referred to as "Salts". These Salts need only dissolving in cold water to be ready for use, saving the dyer the time and trouble of diazotisation.

As the textile material containing azoic coupling component normally also contains excess alkali, and diazo salts are unstable at high pH, it is usually necessary to arrange for neutralization and buffering. The Salts contain the necessary agents to provide the correct conditions for many applications but it is desirable, especially when pad developing, to calculate the quantity of additional "alkali-binding agent" that may be required. Excess acid is avoided as it reduces the rate of coupling.

Dyeing is normally carried out in two stages, impregnation with an alkaline solution of the azoic coupling component being followed by immersion in a solution of the azoic diazo component. The first stage may be carried out on loose fibers, yarn and fabric by batch methods that is, over a period of time, during which the naphthol is absorbed by the fiber, on the normal batch dyeing machines. Fabric may also be impregnated continuously by padding usually followed by immediate drying.

The textile material containing the coupling component (or "naphthol") is then brought in contact with the diazotized base or "salt" solution either in the same piece of equipment in which the naphtholation took place or any suitable processing device. The coupling reaction normally takes place very rapidly. After coupling, the material is well rinsed and then treated at the boil in alkaline detergent solution to remove any loosely held dye and to develop the true hue and maximum fastness properties of the dyed material.

5. Reactive Dyes -

Fiber-reactive dyes are generally used for their high wet fastness and brightness.

Fiber-reactive dyes are capable of forming a covalent chemical bond with textile fibers. These dyes are combined with cellulosic fibers through an alkaline system and are combined with wool, nylon and silk by means of an acid system. The most important area of application is to cellulosic fibers.

The major fiber-reactive groups are:

Monochlorotriazinyl

Dichlorotriazinyl

Monochlorodifluoropyrimidinyl

2,4-Dichloropyrimidinyl

2,4,5-Trichloropyrimidinyl

2,3-Dichloroquinoxaline-6-carbonyl

Chlorobenzothiazole (linked to the dye molecule via -COHN-, -SO$_2$NH-, -NH- or -N=N-)
5-Chloro-4-methyl-2-methylsulphonylpyrimidinyl
Vinylsulphonyl
B-Sulphatoethylsulphonyl
B-Sulphatoethylaminosulphonyl
B-Chloroethylsulphonyl
B-Sulphatopropionamido

The first reactive dyes for cellulosic fibers red on the market in 1956 as a result of the very that dyes containing a dichlorotriazinylamino substituent can be applied to cotton and other cellulosic fibers under midly alkaline conditions, and that the dyes become attached to the fiber by chemical union with the cellulose molecule. It is necessary to bring about reaction with only a few of the many hydroxyl groups in the fiber (even for deep dyeings); mild conditions are suitable for this purpose.

The dichlorotriazinyl-substituted dyes are often so reactive that they can be applied to cellulosic fibers by a cole dyeing process. The second of the two chlorine atoms is less readily replaced than the first, and if at some stage of manufacture of the dye one of them is removed, a monochlorotriazinyl derivative is obtained with lower reactivity than that of the dorresponding dichlorotriazinyl compound; such a dye can still react readily with cellulosic fibers, but requires hot application.

In presence of alkali dyes of both types become attached to the fiber by covalent bonds; as the dye and fiber then form a single chemical entity, the coloured product is highly resistant to wet treatments. Since fiber structure is not significantly affected, the change in fiber qualities is negligible.

Many other reactive systems can be applied similarly, but most have lower reactivity than the dichlorotriazinylamino dyes and, with few exceptions, the dyes need hot conditions for application.

The processes used vary widely, but fall broadly into batch, semi-continuous (or pad-batch) and continuous types. Fixation is effected by means of a variety of alkaline treatments, the temperature used depending on the reactivity of the dye in use. Unfixed dye is removed afterwards in a detergent bath, and finally the dyed material is rinsed with water.

Most reactive dyes are hydrolyzed to some extent during application; the resulting hydroxy derivatives are no longer able to react with cellulose. Some affinity for the fiber remains, but hydrolyzed dyes have low fastness to wet treatments. It is therefore necessary to remove unfixed dye by means of a bath containing soap or other detergent. Reaction takes place mainly with the fiber rather than with water, however, probably due to the rapid adsorption of dye molecules by the fiber.

The reactive dyes for wool are based on a system differing from those used in cellulosic dyes; it has the advantage of not being subject to hydrolysis in the dyebath.

Reactive dyes are normally applied to wool from neutral or weakly acid baths. In order to obtain maximum washing fastness, prolonged boiling, dyeing under pressure, or a final pH of 8.0-8.5 may be required, but these more severe conditions may cause some damage to the fiber.

Reactive dyes for nylon were first introduced in 1959. They are applied in weakly acid conditions, under which reaction with the fiber does not occur, and level dyeings are readily obtained; on treatment with alkali, reaction with the fiber takes place and the resulting dyeings have high fastness to wet treatments. Free amino groups in the nylon fiber provide reactive sites, but there is some evidence suggesting that reaction may also occur with amide groups.

6. Acid Dyes -

Acid dyes are water-soluble anionic dyes that are applied to nitrogenous fibers such as wool, silk, nylon and modified acrylic fibers from acid or neutral baths. Attachment to the fiber is attributed at least partly to salt formation between anionic groups in the dyes and cationic groups in the fiber. A complete range of hues can be obtained, many of them being very bright, and the fastness properties vary from poor to very good.

Wool is dyed in all forms, e.g., loose wool, slubbing, yarn, knitted and woven fabrics, felts and garments. Dyes with good leveling properties find their chief use of yarns and fabrics, but dyes with inferior leveling properties and good fastness to wet processing can be used satisfactorily on loose wool and slubbing.

When applied on silk and nylon, acid dyes vary in properties in much the same way as on wool.

The three main methods for application of acid dyes are characterized by dyebath conditions as follows:

1. Nearly neutral (pH approximately 7.0-5.5)
2. Weakly acid (pH approximately 5.5-3.5)
3. Sulphuric acid (pH 3.5)

The last of these is used on wool, never on nylon.

A special group of acid dyes, called chrome dyes, will react with chromium salts or with bichromate to form a metalized dye. Usually, the metalization is effected subsequent to absorption of dye by the fiber, although with some dyes the metalizing compound is added with the dye to the dyebath. Chroming frequently alters the dyed shade, but enhances fastness to light and to washing.

Some azo dyes may be applied as pre-formed cobalt or chromium complexes.

7. Disperse Dyes -

Disperse dyes are used on acetate, triacetate, nylon, "Qiana" nylon, polyester, polypropylene and polyvinyl chloride fibers and, to a limited degree on acrylic fibers. For some of these fibers they constitute the only practical dye system available. Certain anthraquinone dyes on acetate and triacetate react with oxides of nitrogen in the air; substantive inhibitors are coapplied with these dyes to minimize the shade change which would result from reaction between the gases and the dye.

These dyes are introduced into the dyebath as a fine dispersion. These dispersions of essentially water-insoluble azo, diphenylamine and anthraquinone compounds are produced by grinding with a surfactant or dispersant, e.g., a naphthalene sulfonic acid-formaldehyde condensate or lignin sulfonate.

Fine uniform dispersion is necessary to distribute the dye evenly throughout the dyebath, prevent filtration of the dye by the fibers being dyed and more specifically to present a large surface area of dye particles from which rapid dissolution may take place to replace that taken up by the fiber during dyeing.

Many proprietary carrier compositions or emulsions are offered to enhance absorption of disperse dyes by polyester fibers at the atmospheric boil or their leveling at elevated temperatures in pressurized dyeing vessels. The active agents of such carrier compositions are selected from various aromatic classes including biphenyl, alkyl naphthalenes, chlorinated benzenes, phenyl phenols, butyl benzoate, methyl salicylate, etc.

Dyes containing primary amino groups may be diazotized and developed on the fiber to produce dyeings of varying fastness according to the developers used. This procedure is widely used in the production of blacks.

After the dyeing has been completed, it may be necessary to remove residual carrier by means of (1) heat treatment or (2) scouring the goods in the presence of alkali (NaOH) and a reducing agent ($Na_2S_2O_4$).

8. Basic Dyes -

These are dyes which yield colored cations in aqueous solution. They are often referred to as cationic dyes.

Many of the earliest synthetic dyes, including Perkin's Mauve, the first dye to be produced commercially from coal tar, were basic dyes. Perkin himself was largely responsible for devising the standard methods of application of these dyes to the fibers then available, namely silk, wool and cellulosic fibers (mainly cotton). The appeal of these basic dyes lay in their brilliant hues, some of them being fluorescent. Because of their poor fastness properties, particularly to light, basic dyes were largely superseded following the development of other classes of dyes having superior fastness properties. Basic dyes were retained to a small extent for dyeings where brightness was all-important.

The advent in 1950 of acrylic fibers gave the basic dyes a new lease of life. Many existing basic dyes were found to be much faster to light on these fibers than on natural fibers. This led to the introduction of complete ranges specifically designed for application to acrylic fibers.

Anionic dye-sites have been introduced by fiber manufacturers into nylon and polyester fibers, and some basic dyes have been developed specifically for dyeing one or more of these modified fibers.

Basic dyes are water-soluble, but in most cases solution is facilitated by pasteing the dye with acetic acid and water. Dyebaths require addition of acetic acid.

E. Chemical Assistants Used in Dyeing

In the preceding section, a number of chemicals used as assistants in the dyebath have been mentioned. Some additional general comments on chemical additions to dyebaths is in order. Dyestuffs are seldom if ever applied as the sole constituents of the dyebath. Acids or alkalis may be used to adjust the pH, to aid in dissolving the dye, to speed up the dyeing process or to cause reaction to take place. Salts may be added to accelerate dyeing or to slow it down depending upon the dyeing system. Reducing agents and oxidizing agents are each essential for certain types of dyeing. A variety of surface active agents are employed to wet out the goods, to retard dyeing, to disperse dye, to cause foaming or prevent foaming, to act as emulsifying agents, as anti-migrants, dye leveling agents, etc. There are many hundreds of such products on the market under proprietary names. These agents are listed by use category and by proprietary names in the annual products index ("A buyers guide to U.S. producers and suppliers of dyes, pigments, and chemical specialities for the textile wet processing industry") published by the American Association of Textile Chemists and Colorists. In the annual editions prior to 1976, some indication of the chemical nature of these products is also furnished.

F. Removal of Dyes from Fibers (Stripping)

If after completion of a normal dyeing process the dyeing is found to be off-shade, too dark, uneven or otherwise inadequate, it may be necessary to remove some or all of the dye from the fiber. Depending upon the degree of stripping desired, the chemical nature of the dye and of the fiber, one or more of the following stripping methods are most commonly encountered:

(a) Reductive strip with alkaline sodium hydro-sulfite or acidified zinc sulfoxylate formaldehyde.

(b) An oxidative strip with sodium hypochlorite or sodium chlorite.

(c) A combination of either of the above with a carrier (for polyester).

(d) A carrier/hydrocarbon solvent emulsion under pressure (for polyester).

G. Dyeing Fiber Blends

Very large quantities of finished textiles contain more than one fiber type. Blending of fibers in yarn and fabric is carried out for a variety of reasons, e.g., economics, aesthetics, physical performance characteristics, and to produce special color effects in dyeing. The selection of dyes and proper dyeing methods is a problem for the dyer and when two fibers are in the blend, he is presented with three options, (a) dye one fiber and leave the other white (reserved), (b) dye both fibers but in different or contrasting colors (cross dyed), or (c) dye both fibers the same color (union or solid shade). When the blend consists of more than two different fibers, the options are obviously increased. However, the effect of fiber blends on dyeing effluents is no more than the sum of the effects of dyeing the fibers separately.

Doubtless the specific blend produced in the greatest quantity today is polyester-cotton, and will serve as a case in point. Figure 102 illustrates a continuous process for dyeing such blends and merely combines the pad-steam range for applying vats to cotton with the thermosol range for applying disperse dyes to polyester.

PRINTING

Textile printing is a textile processing area which may contribute significantly to effluents from textile plants but is not within the scope of the present project.

In general, printing carried out by roller or screen methods or by other means, is a method of producing a colored pattern effect on textiles which amounts to localized dyeing. The chief difference between it and ordinary dyeing, other than the mechanical means of transferring the color, is that the dye solutions are more concentrated.

Proper printing viscosity, essential to confinement of the dye to the pattern being reproduced on the textile, is usually achieved by incorporation of thickening agents, e.g., starches and/or natural gums. In some cases water-in-oil and oil-in-water emulsions are used as thickeners. After printing and dye fixation, the thickeners, as well as loose color and any residual chemicals, are removed by washing.

FINISHING

As the term implies, finishing is a final processing operation following preparation and dyeing or printing.

There are scores of finishing agents and many methods by which they may be applied. Again, the AATCC Products Index is a good initial source of information on these products. Basically, finishes are applied to improve either the aesthetics or the utility, or both, of the textile material. The finish may be temporary or durable, may be a simple additive or may bring about chemical modification of the substrate. A finish applied on dyed textiles may affect the appearance of the color to some extent and it can occasionally improve or impair fastness properties.

Some of the commoner finishes are for the following purposes: hand modification (softening or stiffening), dimensional stabilization, durable press, water repellency, flame-retardance, mildew-resistance, moth proofing, static-electricity control.

Finishes sometimes applied by the dyer, usually in the rinse following the dyeing, include:

(a) Antislip agents, e.g., methacrylate resins, polyvinyl alcohols, polyvinyl acetates, to impart body and inhibit yarn distortion.

(b) Antistatic agents, e.g., polyoxyalkylene esters, higher alkylamines, or fatty acid amides which provide temporary antistatic protection to goods.

(c) Atmospheric - Fading Protective Agents, e.g., organic amines, to react with oxides of nitrogen absorbed from the atmosphere. Gases would otherwise react with and alter shade of dyes, particularly anthraquinone blues on acetate.

(d) Fixing Agents, e.g., aliphatic polyamines, resinous copper complexes, dimethylol-ethylene urea resins and other resins, to enhance washing fastness of direct dyes on cellulose fibers and acid dyes on nylon.

(e) Flame Retardants, e.g., halogenated organic compounds, organic phosphorus compounds, to impede flammability.

(f) Lubricants, e.g., wax emulsions, polyoxyethylene - fatty acid derivatives, to facilitate winding, knitting, and sewing.

(g) Softener, e.g., long chain alcohol sulfates, higher alkyl amines and esters, long chain mono and polycations to impart soft hand.

Other finishes are applied in a separate area of the plant subsequent to dyeing. Usually, application is effected by padding or impregnation, frame drying and, sometimes, curing. Included would be durable-press resins, water repellents, soil release and repellent agents, and hand modifiers.

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APPENDIX A

PROCEDURES FOR TRACE METALS ANALYSIS

TRACE METALS

Procedure

Samples were sent to analytical laboratories of six participating companies.

Each laboratory analyzed the samples on or about the 14th day after the samples were prepared. The concentrations of cadmium, chromium, copper, lead and zinc were measured using the standard Environmental Protection Agency method for Extractable Metals[1]. Sample size was decreased from 100 ml to 50 ml to minimize breakage in shipment of large samples. This procedure involved adding hydrochloric acid to the sample which already contained nitric acid added at the time of collection. The solutions were heated for 15 minutes at 95°C. After this treatment solutions were filtered if necessary and the above metals were measured by atomic absorption spectrometry (AAS). Mercury was determined by the EPA cold vapor technique. Triplicate measurements were made on each solution.

Effect of Digestion Procedure

EPA reports[1] that data obtained by the procedure for Extractable Metals "are significant in terms of 'total' metals in the sample, with the reservation that something less than 'total' is actually measured." In order to determine the amounts of metals that might be missed, a sample of exhausted dyebath liquor was also analyzed for Cd, Cr, Cu, Pb and Zn by the EPA method for Total Metals[1]. Table A1 compares results obtained by these two procedures.

The data for this sample did not indicate any significant deficiency in the EPA Extractable Metals procedure for measuring total Cd, Cr, Cu, Pb and Zn in dyebath liquors. This correlated with previous experience of Laboratory E on analyses of other dyebath liquors. While the comparison analyses were not always performed in the same laboratories, subsequent "round-robin"

TABLE A1. COMPARISON OF DIGESTION PROCEDURE

	EPA Extractable Metals (mg/l)			EPA Total Metals (mg/l)		
	Lab C	Lab E	Ave.	Lab A	Lab C	Ave.
Cd	0.02	0.01	0.02	<0.01	0.02	<0.02
Cr	1.8	1.59	1.70	1.9	1.6	1.75
Cu	0.02	0.01	0.02	0.03	0.02	0.03
Pb	<0.2	0.10	<0.15	0.03	0.09	0.06
Zn	0.04	0.05	0.05	0.05	0.05	0.05

analyses showed good interlaboratory correlation so these comparisons are considered valid.

Analysis of Standard Samples

Standards containing known amounts of metals were analyzed by participating laboratories at the beginning and end of the project in order to check accuracy and interlaboratory precision. The first standard was prepared by adding known amounts of metal salts to a dyebath exhaust liquor. Table A2 presents results for the unspiked exhaust liquor while Table A3 gives delta values; i.e., data obtained for the spiked dyebath exhaust liquor minus data obtained in the same laboratory for the unspiked liquor. Laboratories A and C did not analyze the unspiked liquor. Average values from Table A2 were used to correct their data for the original concentrations.

TABLE A2. ANALYSIS OF UNSPIKED DYEBATH LIQUOR NO. 1

All data in mg/l, except for Hg which is μg/l

	B	D	E	F	Ave.
Cd	0.01	----	0.02	----	0.02
Cr	(0.11)*	<0.01	0.03	<0.02	<0.02
Cu	0.08	0.08	0.08	0.08	0.08
Pb	0.05	----	0.02	----	0.04
Zn	0.19	0.22	0.10	0.12	0.16
Hg	----	<1.0	<0.5	<0.5	<0.6

*Data in parentheses not included in calculation of average.

TABLE A3. ANALYSIS OF SPIKED DYEBATH LIQUOR NO. 1

All data in mg/l, except for Hg which is in μg/l. Data corrected for concentrations of metals found in unspiked dyebath liquor

		Laboratory							
	Conc. Added	A	B	C	D	E	F	Ave.	S.D.
Cd	1.00	0.95	0.86	1.00	1.08	1.09	1.00	1.00	0.09
Cr	1.00	0.93	0.89	1.03	1.00	0.96	(0.25)	0.96	0.06
Cu	1.00	0.77	0.92	1.08	0.84	0.84	0.44	0.82	0.21
Pb	1.00	1.05	0.97	1.02	0.80	1.08	0.80	0.95	0.12
Zn	1.00	0.86	0.99	0.88	0.98	1.09	0.88	0.95	0.09
Hg	10.00	7.0	----	6.0	10.0	8.0	(<0.5)	7.8	1.7

Data in parenthese not included in calculation of average and standard deviation (S.D.). Test for excluding data from Reference 2.

There was some question regarding the stability of standard samples prepared from a dyebath exhaust liquor. For comparison, a second standard was prepared by addition of known amounts of metal salts to water distilled in an all-glass still. Results for this standard are shown in Table A4. The concentration levels in the second standard were chosen to be in the ranges encountered in mill samples.

TABLE A4. ANALYSIS OF SPIKED DISTILLED WATER

All results in mg/l, except for Hg which is in µg/l

	Conc. Added	A	B	C	D	E	F	Ave.	S.D.
Cd	0.10	0.10	0.10	0.10	0.04	0.10	0.12	0.09	0.03
Cr	0.50	0.48	0.50	0.47	0.50	0.40	0.52	0.48	0.04
Cu	0.50	0.53	0.50	0.55	0.50	0.51	0.50	0.52	0.02
Pb	1.00	0.98	1.00	0.09	0.80	1.00	0.90	0.96	0.10
Zn	5.00	5.23	6.00	6.10	3.80	5.00	5.20	5.22	0.83
Hg	2.0	1.0	<0.5	0.5	2.5	2.0	2.2	1.5	0.9

Accuracy and precision in Tables A3 and A4 compare favorably with values reported by EPA[1] at comparable levels except in the case of mercury.

ADMI data for mercury are as precise as those reported by EPA but recoveries are lower. Since it is well known that dilute mercury solutions are not stable unless properly preserved, it was suspected that this was the reason for low results. As a result, a special mercury standard solution available from the National Bureau of Standards (No. 1642) was sent to each laboratory for analysis. This solution was stabilized by N.B.S. by the addition of gold.

TABLE A5. ACCURACY AND PRECISION

All data in mg/l, except for Hg which is in µg/l

	EPA Data			ADMI Data		
	Added	Found	S.D.	Added	Found	S.D.
Cd	0.078	0.074	0.018	1.00	1.00	0.09
				0.10	0.09	0.03
Cr	0.407	0.380	0.128	1.00	0.96	0.06
				0.50	0.48	0.04
Cu	0.332	0.324	0.056	1.00	0.82	0.21
				0.50	0.52	0.02
Pb	0.367	0.377	0.128	1.00	0.95	0.12
				1.00	0.96	0.10
Zn	0.310	0.308	0.114	1.00	0.95	0.09
				5.00	5.22	0.83
Hg	9.6	9.1	3.57	10.0	7.8	1.7
	3.40	3.41	1.49	2.00	1.5	0.9

TABLE A6. DETERMINATION OF MERCURY IN NBS STANDARD NO. 1642

1.118 µg/l

Laboratory	Hg Found, µg/l
A	1.5
B	1.0
C	0.5
D	3.2
E	1.0
F	1.8
Ave.	1.5
S.D.	0.95

TABLE A7. STABILITY OF SAMPLES

All results in mg/l, except for Hg which is in μg/l

Sample:	E03001M2		E12003M2		E01020M2	
Date Analyzed:	7/2/75	7/28/75	6/27/75	7/21/75	7/22/75	7/31/75
Cd	0.25	0.25	0.04	0.04	<0.005	<0.005
Cr	0.06	0.06	0.03	0.02	0.03	0.02
Cu	0.27	0.25	0.05	0.03	0.32	0.36
Pb	1.15	0.05	0.05	0.05	<0.05	<0.05
Zn	0.20	0.19	0.26	0.25	1.5	1.6
Hg	1.5	0.1	0.2	----	0.2	0.2

In this case, precision was again comparable to EPA values and accuracy was within the limits of precision.

Stability of Samples

Since it was not always possible to analyze samples exactly 14 days after preparation, several exhausted dyebath liquors were analyzed at various times. No significant differences were noted (Table A7) with the possible exception of mercury. Since dyebath liquors were not specially stabilized for mercury, results for this element may actually be somewhat higher than reported. On the other hand, mercury may be naturally depleted in mill effluents as it was in unstabilized standards.

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APPENDIX B

PROCEDURES FOR BENZIDINE ANALYSIS

BENZIDINE ANALYSIS

Procedure

The method used was an adaptation of the chloramine-T oxidation procedure described in several references (1,2,3); it is described in Table B1. The method differs from the reference only in extracting solvent and extracting techniques. The method was written to be applicable to a variety of dyebath exhaust liquors.

Basically, the method uses ethyl acetate to pre-extract the sample under acid conditions. This removes the ethyl-acetate soluble interfering colors. The remaining aqueous-acid sample is then treated with chloramine-T reagent to oxidize any benzidine present. The oxidation product is extracted with ethyl-acetate and the absorbance determined on the extract. The absorptivity is calculated and compared with the absorptivity of pure benzidine oxidized, extracted and measured in the same manner.

In establishing the method, variations in extracting solvents and pH were investigated in order to minimize the interfering effects of dye bath residues. No single technique was found that would work well for all the types of samples encountered. The interference due to color present might be overcome in some instances by adjusting the method to the sample type. Adjusting the method was not possible in this endeavor because the sample size was limited and only one analysis for benzidine could be performed on each sample.

The Chloramine-T procedure for benzidine is specific. The colored compound formed has a characteristics sharp absorption maxima at 436 nm in ethyl acetate. Other substituted 4, 4'-diaminodiphenyls also produce intense absorption but the wavelengths are shifted sufficiently to differentiate from the benzidine derivative. Benzenoid amines offer no interference. The spectrophotometric absorption curve is shown in Figure B1.

TABLE B1. PROCEDURE FOR THE DETERMINATION OF BENZIDINE IN TEXTILE MILL DYE BATH EXHAUST LIQUORS

1. Place 200 ml of sample in a Squibb type separatory funnel.
2. Add 25 ml of 2N hydrochloric acid. Check for acidity with test paper.
3. Add 50 ml to 100 ml of reagent grade ethyl acetate. The amount used depends on the amount of extractable color present.
4. Shake well; allow the layers to separate; draw off the water layer into a clean beaker and discard the ethyl acetate layer.
5. Return the water layer to the separatory funnel.
6. Add 1 ml of a 10% aqueous solution of Chloramine-T (prepared fresh, weekly), shake, let stand for two minutes.
7. Add 35 ml of ethyl acetate. Shake to extract the color formed.
8. Separate the ethyl acetate layer into a clean beaker and return the acid layer to the separatory funnel.
9. Repeat steps 6, 7 and 8 two more times.
10. Filter the extracts by gravity through dry filter paper into a graduated cylinder. Mix well and record the volume.

Obtain the absorbance of the extract (within 5 minutes) at 436 nm using a 1 cm cell. A full curve from 380-500 nm is desirable. Background color will be present in some samples and a full curve is necessary to correct for background absorption.

Calculation

$$\frac{A_{436} \text{ x ml in end volume of ethyl acetate x } 10^{6}}{\text{ml sample x } a_{std}} = \mu g/l \text{ as benzidine base (MW 184)}$$

a_{std} = the absorptivity of the oxidation product of pure benzidine extracted and measured in a similar manner. Value of a_{std} is approximately 475 but should be determined individually by the analyst.

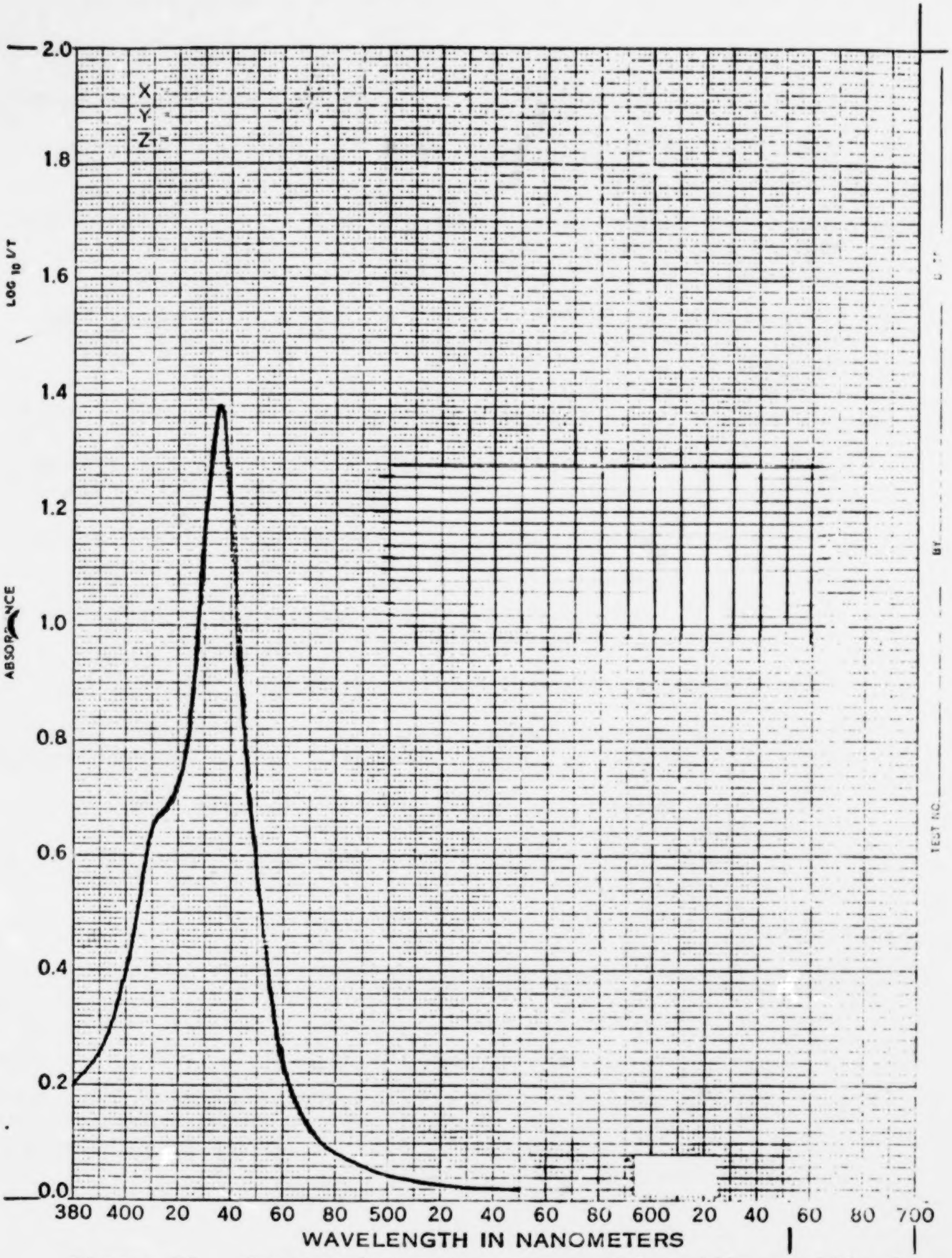

Figure B1. Spectrophotometer curve of benzidine oxidized with chloramine T and extracted with ethyl acetate.

Stability of Sample

Standard samples containing benzidine were sent to the participating laboratories in order to establish the variation in analysis. The prepared samples were found to deteriorate with time, yielding erratic results. Laboratory investigation revealed that hydrochloric acid, reagent grade, added to the samples at the rate of 25 ml per liter produced a stable solution. The actual experiment consisted of storing several solutions of dye bath exhaust liquors, preserved with HCl and unpreserved, containing 120 µg of benzidine per liter, under fluorescent lights for one week. The solutions were then analyzed for benzidine with the following results:

Container	pH	Benzidine, µg/l
Clear Glass Bottle	7.0	82
	Acid-HCl	123
Brown Glass Bottle	7.0	90
	Acid-HCl	121

The sample stored in clear glass at pH 7 dropped to 16 µg/l benzidine at the end of two weeks under fluorescent lights. Another sample in clear glass was stored in the dark for two weeks at pH 7 and dropped only to 111 µg/l benzidine. Data show that HCl preserved samples are stable for a period of two weeks.

CONCLUSIONS

Samples stabilized with HCl were prepared with dye bath exhaust liquor from a dyeing of Direct Black 38 spiked with 500 µg/l of benzidine. A sample of Direct Black 38 contaminated with free benzidine was used to make the dyeings, which accounts for the unspiked analyses listed below.

Sample	Lab 1	Lab 2	Lab 3	Ave.	S.D.
Unspiked	23	29	21	24	4
Spiked with 500 µg/l	588	464	490	514	65

After all of the textile mill samples had been analyzed another final set of standard samples were sent out to two participating laboratories. This time 4 stabilized samples were involved prepared with laboratory dye bath exhaust liquors containing zero, 50, 100 and 200 µg/l benzidine. The results are as follows:

μg/l benzidine added	Lab 1	Lab 2	Ave.
0	0	0	0
50	58	54	56
100	118	80	99
200	264	197	230

The precision indicated is to be expected from the type of samples tested. The standard samples and all of the samples received from the textile mills contained residuals from the dyeing operation. The method will detect a few μg/l when applied to benzidine spiked distilled water, but the dye bath liquors actually tested preclude this kind of sensitivity.

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APPENDIX C

BIODEGRADABILITY PROCEDURE

A. Preparation of Samples

1. Mix dyeing wastewater thoroughly. Collect 12 liters in a glass container.

2. Titrate a 100 ml aliquot to determine the approximate amount of acid or base (NaOH or HCl) required for neutralization. Then, adjust pH to 7.0.

3. Prepare 10 liters of 1% wastewater by adding 100 ml of sample to 9900 ml of distilled water.

4. Add nutrients to the dye solution in the following order:

    a. 10 ml $CaCl_2$ stock solution (27.5 g/l)
    b. 10 ml $MgSO_4 \cdot 7 H_2O$ stock solution (22.5 g/l)
    c. 10 ml $FeCl_3$ stock solution (0.25 g/l)
    d. 10 ml of phosphate buffer

    Stock solution (per liter, 8.5 g KH_2PO_4, 21.75 g K_2HPO_4, 33.4 g $Na_2HPO_4 \cdot 7 H_2O$, 1.7 g NH_4Cl)

    e. 10 ml of yeast extract (2.5 g in 50 ml distilled water)

5. Obtain 250 ml of seed from each pilot unit (see E, below)

    (Unit 1: activated sludge seeded with activated sludge from Durham and fed Durham or Chapel Hill wastewater. Unit 2: as above, but fed wastewater supplemented with the dyeing wastewater). Allow to settle for 15 minutes. Concentrate to 100 ml by removing 150 ml of supernatant.

6. Label two 3-liter flasks as #1 and #2. Use flask #1 to prepare A and B mixtures. Use flask #2 only for C mixture.

7. Dispense into flask 3 liters of dyeing wastewater dilution with added nutrients.

    a. To prepare A series add 30 ml activated sludge. Mix thoroughly. Dispense one liter to each of two 2-liter flasks. Retain remainder for initial analyses.

   b. To prepare B series, proceed as in 7a but inoculate with acclimated activated sludge.

8. Prepare C series in a similar manner, omitting seeding and adding $HgCl_2$ solution (2 g/500 ml).

9. Prepare 10% and 100% series in similar manner by making appropriate dilutions as in Step 3.

10. Cover mouths of flasks loosely with aluminum foil.

11. Enclose flasks in cardboard containers to prevent exposure to light.

12. Place flasks on shaker (∿ 80-90 rev/min).

B. Preparation of Samples for Initial Analyses

1. Filter approximately 250 ml of sample using glass fiber filters (Reeve-Angel) in a filtration apparatus. (In some cases, 0.8 μm pore-size membrane filters were employed).

2. Submit filtered sample for soluble TOC and soluble BOD analysis (BOD's are not performed on C series).

3. Dispense 100-200 ml of unfiltered sample into a brown glass bottle for color analysis.

4. Dispense $\geq$100 ml of unfiltered sample into 125 nalgene bottles, add 1 ml $HgCl_2$ solution for preservation. Submit for analysis of nitrogen forms.

C. Preparation of Samples for Final Analysis

1. After 21 days of incubation at 20 C, remove samples from shaker for final analysis.

2. Prepare and analyze samples as in B.

D. Interim Sampling on 10% Series

1. Remove samples from 10% dilution series (A, B, C) on Monday, Wednesday, and Friday.

2. Filter ∿10 ml of each sample through a glass fiber filter.

3. Submit samples to the laboratory for soluble TOC analysis.

E. Design and Maintenance of Activated Sludge Pilot Units

1. Pilot units were two-liter Nalgene graduated cylinders.
2. To each cylinder was added 600-800 ml of activated sludge from the Northside Wastewater Treatment Plant, Durham, N.C. Bring up to 1500 ml of raw sewage (from Durham).
3. Units were aerated with forced air.
4. The control unit (A, unacclimated) was fed raw sewage daily. For feeding, aeration was discontinued for 30-45 minutes to allow settling of the sludge. The supernatant was then siphoned off and discarded and the remaining volume was restored to 1500 with sewage.

   NOTE: Sewage was warmed to room temperature before addition.
5. The acclimated unit (set #B) was fed raw sewage supplemented with dyeing wastewater.

In each case, the unit was acclimated gradually beginning on day 1 with a 1:20 dyeing wastewater/sewage ratio (5%). The ratio of dyeing wastewater was increased by 5% daily up to 25% (1:4 dyeing wastewater/sewage ratio). Units were acclimated for 1 week prior to biodegradability testing.

APPENDIX D

CHARACTERISTICS OF POWDERED ACTIVATED CARBONS TESTED

The characteristics of the powdered activated carbons tested in the physical-chemical treatment studies described in Section VII are shown in Table D1.

TABLE D1. CHARACTERISTICS OF POWDERED ACTIVATED CARBONS TESTED

Type of Powdered Carbon	Manufacturer	Total Surface area m^2/gm	Iodine No.	Molasses No.
Nuchar D-14	Westvaco	1222	---	---
Nuchar D-16	Westvaco	1294	---	---
Hydro Darco B	ICI-United States	550	550	310
Hydro Darco C	ICI-United States	550	550	310
Hydro Darco 3000	ICI-United States	600	600	310
Darco KB	ICI-United States	1500	1300	630
Darco S-51	ICI-United States	600	600	330

APPENDIX E

SAMPLE CALCULATIONS FOR DETERMINATION OF OZONE CONTENT OF FEED GAS

The gas mixture from the ozone generator was bubbled through two traps containing potassium iodide in series for a period of 2.0 minutes. Aliquots from each of the traps were than titrated with standardized sodium thiosulfate, using starch as an end-point indicator. Since the gas flow rate is known, the ozone content of the feed gas to the reactor can be calculated.

The relevent reactions are:

$$\text{Adsorption:} \quad O_3 + 2I^- + H_2O \rightarrow O_2 + I_2 + 2OH^-$$

$$\text{Titration:} \quad I_2 + 2S_2O_3^{-2} \rightarrow 2I^- + S_4O_6^{-2}$$

From the stoichiometry of these reactions, it can be seen that 1 mole of thiosulfate is equivalent to 0.5 moles of ozone. If 0.1 M $Na_2S_2O_3$ is used as the titrant, then each ml of $Na_2S_2O_3$ is equivalent to

$$1 \text{ ml } Na_2S_2O_3 \times \frac{0.1 \text{ moles}}{\text{liter}} Na_2S_2O_3 \times \frac{0.5 \text{ moles } O_3}{\text{mole } Na_2S_2O_3} \times \frac{48 \text{ gms } O_3}{\text{mole } O_3}$$

$$= 2.4 \text{ mg } O_3 \text{ or } 5 \times 10^{-5} \text{ moles } O_3.$$

Sample Calculation:

Gas Flow Rate - 7 standard cu. ft/hr (scfh)
Absorption Time - 2.0 minutes

Volume titrated - Trap 1 - 50 ml
Trap 2 - 50 ml

Total Volume in trap - Trap 1 - 300 ml
Trap 2 - 300 ml

Titrant ($Na_2S_2O_3$) strength - 0.1 M (2.4 mg O_3/ml)

Volume of titrant required - Trap 1 - 16.75 ml
Trap 2 - 0.10 ml

$$\text{Ozone flow rate} - \frac{16.75 + 0.1 \text{ ml } Na_2S_2O_3}{50 \text{ ml aliquot}} \times \frac{2.4 \text{ mg } O_3}{\text{ml } Na_2S_2O_3} =$$

$$\frac{0.808 \text{ mg } O_3/\text{ml}}{2 \text{ min.}} = 0.404 \text{ mg } O_3/\text{min. absorbed per ml of KI}$$

$$\text{or } 0.404 \times 300 \text{ ml} = 121.2 \frac{\text{mg}}{\text{min}} \text{ absorbed by trap}$$

Hence, the ozone flow rate is 121.2 mg/min or $121.2 \frac{\text{mg}}{\text{min}} \times$

$$\frac{\text{mole}}{48 \text{ mg}} = 2.53 \times 10^{-3} \text{ moles/min.}$$

The ozone content of the gas stream is

$$\frac{2.53 \times 10^{-3} \text{ moles } O_3/\text{min}}{7.0 \text{ cu ft/hr total gas flow}} \times 22.4 \frac{\text{liters}}{\text{mole}} \times \frac{\text{cu ft}}{28.3 \text{ liters}} \times$$

$$\frac{60 \text{ min}}{\text{hr}} = 0.017 \frac{\text{cu ft } O_3}{\text{cu ft gas}} \times 100 = 1.7\% \ O_3$$

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16. ABSTRACT

The report gives results of an examination of the biological, chemical, and physical treatability of wastewaters from selected typical dye baths. Twenty systems, providing a broad cross section of dye classes, fibers, and application techniques, were examined. Wastes, produced using typical formulations on a pilot scale, provided desired control and simulated plant conditions. Raw wastes were characterized. Treated wastes were evaluated for color and total organic carbon (TOC). Biological treatability was examined at several concentrations without seed, with domestic sewage, and with acclimated seed. Wastes generally were compatible with the biological process; color reduction was incomplete. No single treatment was effective for both color and TOC removal. Chemical treatment with ozone decolorized the wastes. Physical treatments included alum, lime, and activated carbon using jar tests. Disperse, vat, and sulfur dyes were most effectively decolorized by coagulation, and carbon was most effective for decolorizing reactive, basic, acid, and azoic dyes. A statistical evaluation of heavy metal content of dye baths and a compendium of dye bath additives and dyeing methods are included.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group	
Pollution	Decoloring	Pollution Control	13B	
Textile Industry	Carbon	Stationary Sources	11E	
Dyeing	Biological Treatment	Total Organic Carbon	13H	06C
Waste Water	Chemical Engineering	TOC Removal		07A
Properties	Ozone		14B	
Treatment	Alums			
Calcium Oxides	Activated Carbon		07B	11G

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